KINETIC STUDY OF CRYSTAL GROWTH FROM SUPERSATURATED DROPLETS

A THESIS

Presented to

The Faculty of the Graduate Division

by

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In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemical Engineering

Georgia Institute of Technology

February, 1975

KINETIC STUDY OF CRYSTAL GROWTH FROM
SUPERSATURATED DROPLETS

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Date Approved by Chairman: Feb. 12, 1975

ACKNOWLEDGEMENTS

The author wishes to express his special gratitude to Dr. Clyde Orr, Jr., his thesis advisor, for the useful research experience acquired while working under his supervision for a number of years. In particular, the author is deeply indebted to him for his encouragement and guidance throughout the course of the work. Very valuable comments and suggestions rendered by Dr. Henderson C. Ward and Dr. Homer V. Grubb, who served as members of the reading committee, are also gratefully acknowledged. In addition, the author is very grateful to Mr. Edward Y. H. Keng for his continued support and suggestions.

The author acknowledges the valuable assistance of Mr. Eugene Weaver in the experimental work on homogeneous nucleation from supersaturated solutions. Sincere appreciation is also extended to Mrs. Nancy Price for the typing of this manuscript.

The author appreciates the research assistantships he received through the Engineering Experiment Station for studies supported by the U. S. Public Health Service under Grants AP 00816 and EC00338. The author is also grateful for the teaching assistantship and scholarship arranged by Dr. Grover L. Bridger.

Particular appreciation is expressed to Dr. Waldemar T. Ziegler for his valuable guidance and advice during the course of the graduate studies.

It is also a pleasure to acknowledge the supports of friends: Dr. Richard R. C. Chu, Dr. Kuei-Yen Hsu, Mr. Nan Wei and Mr. Ta-Yeh Jerry Fang, all of whom helped in many and varied ways during the preparation of this work.

The author is indebted to his parents, Mr. and Mrs. Chuan-Shui Wen, for their constant support and inspiration to achieve higher academic goals. Finally, the author wishes to thank his wife, Mrs. Fu-Yuan Wen, for her encouragement and sacrifice at all times so that this work could be completed.

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SUMMARY

Nucleation processes can be described mathematically by the Zeldovich-Frenkel equation. Solutions of the equation lead to two relaxation times: the relaxation time to approach the steady-state cluster distribution and the relaxation time to achieve the occurrence of the critical cluster. Theoretical investigation indicates that, for nucleation from aqueous solutions, the induction time of homogeneous nucleation is governed by the latter, while the former plays a very important role in heterogeneous nucleation. Relationships between relaxation time and the conditions of supersaturation were derived for several possible situations.

Homogeneous nucleation of crystals from aqueous sodium chloride solutions was studied with a new droplet technique. Droplets of very small size were dispersed as aerosols instead of into oil. The relaxation time was determined with a light extinction method instead of tedious and inaccurate counting of the frequency of crystallization among droplets under magnification. Using a simple relationships between the relaxation time and the homogeneous nucleation rate, the kinetic constant and the crystal-solution interfacial free energy were found to be 10^{48} cm^{-3} sec^{-1} and 115.9 erg cm^{-2}, respectively.

Heterogeneous nucleation and the effect of soluble impurities on the nucleation processes were also studied. The concept of relaxation times again provided an effective approach to the solution of these

problems. A detailed mechanism which includes adsorption, surface diffusion, and two-dimensional clustering processes was developed from induction time measurements for aqueous solution droplets nucleating on various surfaces for the heterogeneous nucleation of crystals from solutions. Induction time measurements also indicate that lead ions poison only heterogeneous clustering in an aqueous sodium chloride solution by changing the binding energy for two-dimensional nucleation.

Crystal growth is a two-dimensional process. The behavior of solute molecules on a crystal surface under supersaturated conditions can also be described by the Zeldovich-Frenkel equation. From a most general treatment of nucleation kinetics, the two-dimensional nucleation theory was re-examined by including nonsteady-state effects. Based on the relaxation-time approach, a new relationship between growth rate and supersaturation has been attained for crystal growth from solution.

To test the new theory, an experimental investigation of the growth rate of crystals from aqueous sodium chloride solutions at controlled supersaturations was performed using the droplet method. The droplet method has the advantage that with it a wide range of supersaturations can be conveniently achieved by adjusting the ambient humidity conditions. Using data from experimental measurements and data from the literature, the new relationship between the growth rate and the supersaturation condition was confirmed for aqueous sodium chloride and aluminum potassium sulfate systems at both low and high supersaturations.

PART I

NUCLEATION

CHAPTER I

INTRODUCTION

General Background

Phase transformation is a natural phenomenon. When a new phase is formed within a metastable mother phase, phase transformation takes place through the processes of nucleation and growth. The daughter phase is created first in the form of microscopic molecular aggregates, or clusters, by random fluctuations. Subsequent growth of the stable clusters, the nuclei, by accreting additional molecules enables the new phase to attain macroscopic size.

Nucleation, whether from a vapor, liquid, or solid mother phase, depends upon the purity of the system. In the absence of foreign surfaces or other catalytic agents, nuclei are formed randomly in the mother phase; phase transformation is then said to have been initiated by homogeneous nucleation. When nucleation is induced by a foreign surface or other agent, the phase transformation is termed heterogeneous nucleation.

Nucleation processes are of interest in many scientific investigations and important in numerous engineering applications. For example, it has long been of interest to the field of atmospheric science as nucleation must precede the formation of rain, fog, and snow.[1] Recently, it has become evident that both homogeneous and heterogeneous nucleation play very important roles in photochemical

smog formation.[2,3] Application of nucleation theory in attempting to explain condensing nozzle flow is extensive, with comprehensive reviews of the subject having appeared.[4,5] Nucleation is also involved in solid-state physics,[6] thin films,[7,8,9] solution crystallization,[10,11,12] solidification of metals and alloys,[6] cavitation and boiling,[6,13] as well as many biological processes.[10]

Although the first nucleation study can be dated back more than two hundred years when the German physcist Gabriel Fahrenheit initiated a systematic study of how water freezes into ice, the theory of nucleation may be considered to have begun in 1926 with the work of Volmer and Weber.[14] The so-called classical nucleation theory, based on Volmer and Weber's work, has also been developed on a kinetic basis.[15,16] The problem is viewed as a single-current rate process in which clusters and nuclei are developed in the metastable phase by unit additions of molecules of monomer. The basic postulate of the classical nucleation theory is that the free energy of formation of the clusters may be described in terms of macroscopic thermodynamic properties of the mother and the daughter phases. Actually, the clusters and the nuclei are comprised only of a few molecules. The classical theory therefore experiences difficulties when parameters such as the interfacial free energy and density of these small clusters are taken into account.

For years verification of nucleation theory was sought through experiments on the critical condensation of vapors, especially water vapor.[17,18] Disregarding the doubtful postulates employed, classical theory seemed to agree rather well with experimental data, even though the approximate nature of the experiments precluded really precise

comparison. Since all physical quantities, including interfacial free energy are well known for theoretical prediction of critical supersaturation for water droplets, the agreement of the observations, especially those of Volmer and Flood,[19] with classical theory caused the theory to stand for many years as the foundation of knowledge of nucleation.

Unfortunately the validity of the classical theory came to an end when statistical mechanical contributions, mainly translational and rotational, to the free energy of formation of the clusters were introduced. Lothe and Pound[20] found, by including such contributions, the predicted rate of nucleation could be greater by a factor of 10^{17} in the case of homogeneous nucleation of water droplets from vapor at $300^{\circ}K$. In order to restore agreement between theory and experiment, ideas arose such as discounting replacement factor[21,22] or increasing the interfacial free energy by some 15 to 20 per cent for microscopic cluster and nuclei.[23,24] Due to the complexity of the problem and the lack of convincing models, disagreements appear constantly in the literature,[21,22,25] and controversy over the replacement factor caused by the statistical mechanical contributions is far from settled.

Agreement between theory and experiment is also hindered by the experiment itself. Experimental studies of nucleation in the vapor phase are mostly accomplished by an expansion process. The vapor is cooled by expansion either in cloud chambers[19,26-29] or in nozzles.[30,31] Quantitative testing of nucleation theory is not entirely feasible due to limitations and uncertainties in each of these methods.[4,5,32] With an expansion cloud chamber method, including that employed by

Volmer and Flood,[19] the expansion may be far from ideal owing to turbulence, flow reversal, and transient heating of the walls of the chamber. This makes direct measurement of nucleation rates over different supersaturations extremely difficult since theory predicts the homogeneous nucleation rate in condensation will rise from a very low to a very high value over an extremely narrow supersaturation range. Only critical supersaturation data are obtained in cloud chamber experiments.[17] Nozzle methods share one of the problems of the cloud chamber method in that delay effects owing to droplet growth on the initial nuclei must be carefully considered. These methods would be more reliable if detecting techniques were improved so that the number and size of nuclei could be measured for smaller clusters than can now be done.

Verification of nucleation theory through the nucleation of crystals from a liquid is also employed extensively.[33,34] Since a critical cluster is thought to be composed of only about 100 molecules, any impurity larger than the critical cluster may catalyze the nucleation process. Meaningful experimental data emerge only after these undesired catalytic effects are eliminated. In practice a body of liquid suspends about 10^6 foreign nuclei per cubic centimeter. An apparently effective technique for eliminating those contamination effects, as suggested by Vonnegut,[35] is to disperse the liquid into droplets of extremely small volume. The active foreign nuclei are thereby confined to a small proportion of the droplets so that their effect can be negligible. In practice, liquid droplets are generally dispersed within a suitable medium, usually an oil, which is assumed

to be inert. Supersaturation within the droplets is achieved by supercooling the system. The rate of nucleation can then be directly determined by measuring the frequency of the nucleation events.

This droplet technique has limitations and uncertainties as well as merits. For example, generation and uniform control of the supersaturation condition for the system by supercooling is not an easy task. Droplet size must be extremely small to ensure impurity-free conditions. Counting the frequency of crystallization among small droplets under magnification to determine the rate of nucleation is very tedious and inaccurate, especially when the nucleation rate is high. Furthermore, although the medium itself may be inert, it may contain impurities which catalyze nucleation at the oil-droplet interface.

The droplet technique has had considerable success in studies involving the homogeneous nucleation of some one-component liquids.[34-38] Unfortunately the technique has not worked well in the past for aqueous solution systems.[39-43] Kinetic constants obtained in previous studies lie in the range of 10 to 10^6 cm^{-3} sec^{-1} which are at considerable variance with value 10^{33} cm^{-3} sec^{-1} predicted by classical nucleation theory.[16] Further work to narrow the discrepancies between theory and experiment is, of course, required.

Scope of the Research Effort

Both homogeneous nucleation and heterogeneous nucleation processes can be described mathematically by the Zeldovich-Frenkel equation.[44,45] Solution of the equation leads to two relaxation

times: the relaxation time to approach the steady-state cluster distribution and the relaxation time to achieve the occurrence of the critical cluster. Theoretical investigation indicates that, for nucleation from supersaturated aqueous solutions, the induction time of homogeneous nucleation is governed by the latter, while the former plays a very important role in heterogeneous nucleation. Relationships between the relaxation time and the supersaturation condition were therefore derived for several possible situations.

Homogeneous nucleation of aqueous solutions was studied with an improved droplet technique, the new technique being designed to overcome the difficulties previously experienced. Droplets of very small size were dispersed into the atmosphere as aerosols instead of into oil. The effects of foreign surfaces and the droplet-medium interface, if any, were thus minimized. Supersaturation conditions for the droplets could also be better controlled through regulation of equilibrium humidity conditions. From the concept of relaxation times as employed in this research, homogeneous nucleation rates were obtained in a much easier manner over a wider range, enabling closer verification of homogeneous nucleation theory for an aqueous solution system through evaluation of the kinetic constant and the cluster-solution interfacial free energy.

Heterogeneous nucleation and the effect of soluble impurities on the nucleation processes were also studied. Catalysis due to the presence of foreign surfaces is probably the most common situation encountered in nature as well as in the laboratory, and soluble impurities have long been recognized as influencing the crystallization

process.[46] The exact nature of these phenomena is not well understood, and very few systematic experimental studies have been reported.[47,48] The concept of relaxation times again provided an effective approach to the solution of these problems. A detailed mechanism which includes adsorption, surface diffusion, and two-dimensional clustering processes was developed from induction time measurements for aqueous solution droplets nucleating on various surfaces for the heterogeneous nucleation of crystals from supersaturated solutions.

An aqueous sodium chloride solution system was chosen for the present investigation because it offered very suitable physical properties, including those of hygroscopicity and solubility. Small sodium chloride particulates are most important condensation nuclei.[1] Hopefully the results of this research can lead to a better understanding of the behavior of condensation nuclei in the atmosphere.

CHAPTER II

THEORETICAL CONSIDERATIONS

Nucleation is a molecular process. Present theory relating to it is based on the idea that molecular aggregates, the clusters, of different sizes exist in dynamic equilibrium with the supersaturated mother phase. The clusters are considered to grow or to decay according to statistical fluctuations. Following Einstein's fluctuation theory, the probability of such fluctuations is a function of the free energy of formation of the clusters in the system. For any supersaturated mother phase, there exists a cluster of critical size at which the free energy of formation is maximized. Further growth of the critical cluster is therefore energetically favorable. The formation of a new phase occurs spontaneously once the cluster reaches its critical size.

General Formulation of Nucleation Process

According to nucleation theory, clusters of different sizes are the result of a sequence of bimolecular reactions.[15] Postulating that a cluster α_x, containing x molecules, can undergo transition only to its next nearest neighbors α_{x+1} or α_{x-1} by adding or losing a monomer α_1, the process may be represented by the scheme[15,16]

$$\alpha_1 + \alpha_1 = \alpha_2$$

$$\alpha_2 + \alpha_1 = \alpha_3$$

$$- \quad - \quad - \quad -$$

$$\alpha_x + \alpha_1 = \alpha_{x+1} \qquad \text{(I-1)}$$

$$- - - -$$

$$\alpha_{x_c} + \alpha_1 \rightarrow \alpha_{x_{c+1}}$$

where x_c represents the number of the molecules in a cluster of critical size.

Assuming that the degree of supersaturation in the system is constant during the process, the probability, $P(x,t)$, of finding a cluster to be of size x at time t may be described by a partial differential equation similar to the Zeldovich-Frenkel equation[44,45,49]

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{D(x)\, P^{o}(x)\, \frac{\partial}{\partial x}\left[\frac{P(x,t)}{P^{o}(x)}\right]\right\} \qquad \text{(I-2)}$$

with initial and boundary conditions

$$\begin{aligned} &P(1,t) = P^{o}(1) = 1 && \text{for } t \geq 0 \\ &P(x,0) = 0 && \text{for } x > 1 \\ &P(x,t) = 0 && \text{for } x > x_c \end{aligned} \qquad \text{(I-3)}$$

Here $D(x)$ is the flux of the monomers joining the cluster of size x. It is assumed to be proportional to $S(x)$, the surface area of the cluster, through the relationship[49]

$$D(x) = \nu S(x) \qquad \text{(I-4)}$$

where ν is a frequency factor. $P^{o}(x)$ is the probability of finding a cluster to be of size x at equilibrium conditions; it is given by the thermodynamic relation[50]

$$P^{o}(x) = \exp\left[-\frac{\Delta G(x)}{kT}\right] \qquad \text{(I-5)}$$

where $\Delta G(x)$ is the Gibb's free energy of formation of the cluster of size x in the supersaturated mother phase, k the Boltzmann constant, and T the absolute temperature.

Many investigations have been devoted to the solution of equation (I-2) with its initial and boundary conditions (I-3) subject to various approximations.[24,44,51-59] The following summarizes the analytical solutions existing in the literature:

Zeldovich:[44]

$$P(x,t) = P_{st}(x) \exp\left[-\tau_1/t\right] \qquad \text{(I-6)}$$

Wakeshima;[53] Feder, et al.;[24] Chakraverty:[49]

$$P(x,t) = P_{st}(x)\left[1 - \exp(-t/\tau_1)\right] \qquad \text{(I-7)}$$

Kashchiev:[57]

$$P(x,t) = P_{st}(x)\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2 t/\tau_1)\right] \qquad \text{(I-8)}$$

The steady-state probability distribution, $P_{st}(x)$, is given by the relationship[44]

$$P_{st}(x) = Z\,P^{o}(x) = Z \exp\left[-\frac{\Delta G(x)}{kT}\right] \qquad \text{(I-9)}$$

where Z is the Zeldovich factor. The relaxation time to approach the steady-state cluster distribution, τ_1, can be expressed by[49,57]

$$\tau_1 = - \frac{\lambda k T}{D(x_c)\left\{\frac{d^2[\Delta G(x)]}{dx^2}\right\}_{x=x_c}} \qquad \text{(I-10)}$$

where λ is a numerical factor having a value between 0.5 and 5, depending upon the approximations made.

Equations (I-6), (I-7), and (I-8) indicate that the solution of the probability distribution for the cluster, $P(x,t)$, is composed of two factors: the steady-state probability distribution $P_{st}(x)$ and its transient effect due to the relaxation time τ_1. $P_{st}(x)$ is time-independent if the supersaturation condition of the system remains invariant. The solution shows that at the moment $t = 5\tau_1$, $P(x,t)$ reaches 99 per cent of its steady-state value. Consequently, a steady-state probability distribution for the cluster concentration within the system can be assumed after this transient period.

Relaxation Times and Homogeneous Nucleation from Solution Thermodynamics of Cluster Formation

The thermodynamic aspects of the formation of homogeneous clusters have been discussed extensively by many investigators.[60-65] Since the required interfacial free energy is not known, the exact shape of the critical cluster cannot be calculated from the Gibbs-Wulff theorem.[66] If a spherical cluster of radius r is assumed, the free energy of formation of the cluster can be expressed as[6]

$$\Delta G(r) = \Delta G_s + 4\pi r^2 \gamma + 4/3\ \pi r^3 \Delta G_v \qquad \text{(I-11)}$$

where ΔG_s is the statistical mechanical contribution to the cluster

free energy and is essentially independent of cluster size.[6] Here γ is the cluster-mother phase interfacial free energy and ΔG_v the free energy change per unit volume of the stable daughter phase. For the nucleation of crystals from solution[43]

$$\Delta G_v = - \frac{kT}{\Omega} \ell n \, (a_1/a_o) \qquad \text{(I-12)}$$

where a_1 and a_o are the activities of the solute at supersaturated and saturated conditions, respectively, and Ω is the molecular volume of the solute given by

$$\Omega = \frac{M}{\rho N} \qquad \text{(I-13)}$$

where M is the molecular weight of the solute, ρ the density, and N the Avogadro number.

The free energy of formation of the cluster can also be expressed in terms of the number of molecules in the cluster by the expression[6,49,57]

$$\Delta G(x) = \Delta G_s + ax + bx^{2/3} \qquad \text{(I-14)}$$

where the constants a and b are given by

$$a = - kT \, \ell n \, (a_1/a_o) \qquad \text{(I-15)}$$

$$b = \gamma \, (4\pi)^{1/3} \, (3\Omega)^{2/3} \qquad \text{(I-16)}$$

The value of $\Delta G(r)$ goes through a maximum as the cluster increases to its critical size. Hence the radius of the critical cluster may be calculated by letting $[d\Delta G(r)/dr]_{r=r_c} = 0$. Thus

$$r_c = \frac{2 \gamma M}{\rho N \, k \, T \, \ell n \, (a_1/a_o)} \qquad \text{(I-17)}$$

Similarly, there can be obtained

$$x_c = \frac{32 \pi M^2 \gamma^3}{3 \rho^2 N^2 k^3 T^3 \ell n^3 (a_1/a_o)} \qquad \text{(I-18)}$$

Relaxation Time to Approach the Steady-State Homogeneous Cluster Distribution

While the problem of the time lag is of much interest in adiabatic expansion experiments with vapors, most calculations of the relaxation time to approach the steady-state cluster distribution, τ_1, have been from experiments involving homogeneous nucleation of droplets from the supersaturated vapor phase.[24,51-56,58] It is generally agreed that τ_1 must be of the order of a microsecond at ordinary conditions for homogeneous nucleation to occur.

A good estimation of the relaxation time τ_1 is not available for homogeneous nucleation from condensed phases. However, according to the theory of absolute reaction rates,[67] the flux of monomers joining a cluster of size x can be expressed as[16]

$$D(x) = \left[\frac{kT}{h} \right] \exp \left[- \frac{\Delta U}{kT} \right] S(x) \qquad \text{(I-19)}$$

where h is Planck's constant and ΔU the activation energy for diffusion of monomers in the volume of the condensed phase.

The situation for calculating the monomer flux for a nucleation process becomes even more complicated when a crystalline cluster is considered. The monomers arriving at the surface of a cluster must experience a particular kind of activated process before they can be incorporated into the crystalline lattice. Therefore D(x) should include

a function f to account for the growth mechanism of crystalline clusters.[68,69] The mechanism of crystal growth from solution will be discussed in Part II of this thesis. If two-dimensional nucleation theory is employed for this purpose, the function f takes the form[70]

$$f = A_2 \exp\left[-\frac{B\,\gamma_a^2}{\ell n(a_1/a_o)}\right] \qquad \text{(I-20)}$$

where A_2 and B are constants and γ_a the binding energy for two-dimensional nucleation.

If a spherical critical cluster is assumed, substituting equations (I-14), (I-19) and (I-20) into equation (I-10) yields

$$\tau_1 = \frac{2\,\lambda h\,\gamma}{A_2 k^2 T^2 \ell n^2(a_1/a_o)} \exp\left[\frac{\Delta U}{kT}\right] \exp\left[\frac{B\,\gamma_a^2}{\ell n(a_1/a_o)}\right] \qquad \text{(I-21)}$$

Equation (I-21) indicates that for condensed phases, τ_1 could be a few orders greater than for vapor phases due to the fact that substantial activation energy of diffusion of monomer in the condensed phases is included. However, except for very viscous solutions, it is reasonable to assume a fraction of a second[48] for the relaxation time to approach a steady-state cluster distribution in the homogeneous nucleation of aqueous solutions. Such times can be neglected in this study.

Relaxation Time to Achieve the Occurrence of the Critical Homogeneous Cluster

The appearance of the daughter phase within a supersaturated phase of confined volume will not take place until a "real" critical cluster exists. The appearance of such a real critical cluster within

the system does not necessarily follow immediately after a transient period. The steady-state probability of finding a critical cluster could be extremely small if the supersaturation is less than a certain critical value. The time interval between the end of the transient period and the onset of nucleation is, of course, important in the kinetics of the nucleation process. Since an exact expression for this time interval is not available,[11,12,33,71] the matter is considered in the following treatment.

Let a condensed system composed of small droplets be considered which are to experience homogeneous nucleation under constant supersaturation. Assuming the relaxation time τ_1 relatively small and negligible, then the probability of finding a cluster to be of critical size can be approximated in relation to its equilibrium probability by solution of the Zeldovich-Frenkel equation. Thus equations (I-6), (I-7),(I-8) and (I-9) give

$$P(x_c) = \frac{N(x_c)}{N_1} = \exp\left[- \frac{\Delta G(x_c)}{kT} \right] \qquad \text{(I-22)}$$

where $N(x_c)$ and N_1 are the numbers of critical clusters and monomers per unit volume of the supersaturated phase, and $\Delta G(x_c)$ the free energy of formation of the critical cluster. It should be noted that for homogeneous nucleation in a small droplet system, the Zeldovich factor does not apply due to the facts that the formation of only one critical cluster per droplet is expected to cause complete phase transformation within the droplet and that the probability distribution of the clusters in one droplet will not be affected by the

occurrence of nucleation of others. This implies that after the transient period, no probability flux is to be considered.

A probability theorem states that if the probability of an occurrence in a single trial is p, the probability of an event not occurring in n trials is[72]

$$1 - W = (1 - p)^n \tag{I-23}$$

where W is the probability that the event will occur in n trials. If a supersaturated droplet is under consideration, the probability that homogeneous nucleation will occur within the droplet in time t becomes

$$W = 1 - [1 - N_1 VP(x_c)]^{D(x_c)t} \tag{I-24}$$

where V is the volume of the droplet and $D(x_c)$ the flux of monomers joining the critical cluster. The product $N_1 VP(x_c)$ is the total probability of finding a critical cluster in a droplet, while $D(x_c)t$ is considered to be the total number of trials tending to nucleate the droplet in the time interval t. Since $N_1 VP(x_c)$ is very small compared with unity, equation (I-24) may be simplified to

$$W = 1 - \exp [-D(x_c)N_1 VP(x_c)t] \tag{I-25}$$

The steady-state nucleation rate, J, is generally defined as the product of the steady-state concentration of the critical cluster and the flux of the monomer joining the critical cluster. By neglecting the Zeldovich factor, this gives

$$J = D(x_c)N(x_c)$$

$$= A_1 \exp\left[-\frac{\Delta G(x_c)}{kT}\right] \qquad \text{(I-26)}$$

where A_1 is the product of $D(x_c)$ and N_1 and is called the pre-exponential factor of the homogeneous nucleation rate equation. With this definition of A_1, equation (I-25) becomes

$$W = 1 - \exp\left[-A_1 V P(x_c) t\right] \qquad \text{(I-27)}$$

Equation (I-27) may be rewritten as

$$W = 1 - \exp\left[-t/\tau_2\right] \qquad \text{(I-28)}$$

where τ_2 is, therefore, the relaxation time to achieve the occurrence of a critical homogeneous cluster within the supersaturated droplet and is given by the relationship

$$\tau_2 = \frac{1}{A_1 V \exp\left[-\frac{\Delta G(x_c)}{kT}\right]} \qquad \text{(I-29)}$$

or it can be written that

$$J V \tau_2 = 1 \qquad \text{(I-30)}$$

Equation (I-30) offers a simple relationship between the relaxation time τ_2 and the homogeneous nucleation rate. It is to be noted that only the empirical proportion of $J \propto \tau_2^{-1}$ was assumed prior to this study.[11,12,43,71]

If an induction time, θ_2, is defined to be the time in which a droplet is 99% certain to nucleate or that 99% of the droplets in the system will nucleate, then there is obtained

$$\theta_2 = 5\tau_2 \tag{I-31}$$

or

$$\ell n\ \theta_2 = -\ \ell n\ \left(\frac{A_1 V}{5}\right) + \frac{\Delta G(x_c)}{kT} \tag{I-32}$$

Substituting equations (I-14), (I-15),(I-16) and (I-18) into equation (I-32) gives the relationship

$$\ell n\ \theta_2 = -\ \ell n\ K_1 - \ell n\ (V/5) + \frac{16\ \pi\ \gamma^3 M^2}{3\rho^2 N^2 k^3 T^3}\ \ell n^{-2}(a_1/a_o) \tag{I-33}$$

where

$$\ell n\ K_1 = \ell n\ A_1 - \frac{\Delta G_s}{kT} \tag{I-34}$$

and K_1 is defined as the kinetic constant for homogeneous nucleation.

Equation (I-33) indicates that a linear relationship between $\ell n\theta_2$ and $\ell n^{-2}(a_1/a_o)$ should be obtained with homogeneous nucleation experiments involving aqueous solution droplets at constant temperature. Since the molecular weight and the density can be assumed constant for a particular system, the interfacial free energy of the critical cluster can be calculated from the slope of a straight line plot. The kinetic constant K_1 similarly can be evaluated for verification of homogeneous nucleation theory.

Relaxation Times and Heterogeneous Nucleation from Solution

In heterogeneous nucleation, the clustering of molecules takes place on a foreign surface immersed in the supersaturated mother phase. From the assumptions culminating in the Zeldovich-Frenkel equation and its initial and boundary conditions, it is clear that equations (I-6), (I-7), and (I-8) may also be applied to express the probability distribution of a heterogeneous cluster. If an asterisk,*, is used to indicate that the quantities involved refer to the heterogeneous nucleation situation, then equations (I-6),(I-9), and (I-10) can be rewritten in the forms

$$P^*(x^*,t) = P^*_{st}\ (x^*_c)\ \exp\left[-\tau^*_1/t\right] \qquad \text{(I-35)}$$

$$P^*_{st}(x^*) = Z^*\ \exp\left[-\frac{\Delta G^*(x^*)}{kT}\right] \qquad \text{(I-36)}$$

$$\tau^*_1 = -\frac{\lambda\ k\ T}{D^*(x^*_c)\left\{\dfrac{d^2[\Delta G^*(x^*)]}{dx^{*2}}\right\}_{x^*=x^*_c}} \qquad \text{(I-37)}$$

Since the quantities involved are directly affected by interactions among the cluster, the supersaturated mother phase, and the foreign surface, it will be necessary to consider some important parameters before proceeding further with the discussion.

Cluster Shape Factor

The existence of a foreign surface changes the shape of the cluster and, therefore, affects the free energy of formation and the size of the critical cluster. If the same condition of supersaturation

is taken for both the homogeneous nucleation process and the heterogeneous nucleation process, then it can be shown that the free energy of formation and the size of the critical clusters of the two processes are related by[73]

$$\Delta G^*(x_c^*) = \Phi \Delta G(x_c) \qquad \text{(I-38)}$$

$$x_c^* = \Phi x_c \qquad \text{(I-39)}$$

where the cluster shape factor Φ accounts for the effect of the foreign surface and is generally a function of the cluster-foreign surface contact angle. Expressions for Φ have been derived by assuming various shapes of the clusters at different foreign surface conditions.[6] If the cluster is assumed to be isotropic and of flattened hemispherical symmetry on a clean flat surface, it has been shown that[73]

$$\Phi = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \qquad \text{(I-40)}$$

where θ is the equilibrium contact angle between the cluster and the foreign surface. Since $-1 \leq \cos\theta \leq 1$, $0 \leq \Phi \leq 1$, and the presence of the foreign surface reduces the free energy of formation and the size of the critical cluster except in the limiting case when $\theta = 180^\circ$.

Flux of Monomers to the Cluster on a Surface

The kinetic nature of the clustering may also be influenced by the presence of the foreign surface. Logically the process of cluster formation may occur by the direct addition of monomers from the supersaturated mother phase, by surface diffusion of the adsorbed monomers on the foreign surface, or by the two mechanisms combined.

The choice of these distinct possible mechanisms depends upon the parameters related to the interactions between the monomers and the foreign surface, namely, upon the activation energy of surface diffusion of the monomers, ΔU_D, and the activation energy of desorption of the monomer from the foreign surface, ΔU_{des}.[74] Therefore the flux of the monomers to the surface of the critical heterogeneous cluster, $D(x_c^*)$, may be in accordance with different expressions in different situations:

1. $\Delta U_D >> \Delta U_{des}$. In this case the monomers are considered to add to the heterogeneous cluster directly from the supersaturated mother phase by volume diffusion. If a flattened, hemispherical, isotropic critical cluster is assumed, the volume-diffusion-controlled monomer flux, $D_v^*(x_c^*)$, is given by[68]

$$D_v^*(x_c^*) = \frac{1 - \cos\theta}{2} D(x_c) \qquad \text{(I-41)}$$

in which $(1 - \cos\theta)/2$ accounts for the reduction in surface area of the heterogeneous critical cluster in comparison to the surface area of the homogeneous critical cluster at the same supersaturation condition.

2. $\Delta U_D << \Delta U_{des}$. Here the critical heterogeneous cluster is formed by activated surface diffusion of the monomers on the foreign surface. The monomers are first adsorbed onto the foreign surface, then they perform a two-dimensional random walk on the surface. Some of them encounter a heterogeneous cluster and are incorporated into it before being dispersed into the supersaturated mother phase. The migration of the monomers tends to be toward the periphery of the base of the cluster. Again, if an isotropic and semi-hemispherical critical

cluster is assumed, then the surface-diffusion-controlled monomer flux, $D_s^*(x_c^*)$, can be expressed in the form[74,75]

$$D_s^*(x_c^*) = 2 \pi r_c^* \text{ Sin } \Theta \, n_s \, \bar{\delta} \, \bar{\omega} \exp \left[- \frac{\Delta U_D}{kT} \right] \qquad \text{(I-42)}$$

where r_c^* is the radius of curvature of the critical cluster, n_s the surface concentration of the adsorbed monomers, $\bar{\delta}$ the lattice parameters of the foreign surface, and $\bar{\omega}$ a vibrational frequency factor.[6]

3. $\Delta U_D \simeq \Delta U_{des}$. In this case both the volume diffusion mechanism and the surface diffusion mechanism are taken into account. The monomers join the heterogeneous cluster both by direct addition from the supersaturated mother phase and by surface diffusion over the foreign surface. It has been shown that the latter mechanism is more favorable by the factor $\exp (\Delta U_{des} - \Delta U_D)/kT$.[74] The total flux of the monomers can therefore be expressed by combining both mechanisms described previously, that is

$$D^*(x_c^*) = D_v^*(x_c^*) + D_s^* (x_c^*) \qquad \text{(I-43)}$$

It is clear that for the formation of a crystalline heterogeneous cluster, the monomer flux, $D^*(x_c^*)$ should also include a function f which can describe the growth mechanism of the cluster. A function having the form of equation (I-20) can therefore be postulated for the two-dimensional growth of a heterogeneous cluster.

Relaxation Time to Approach the Steady-State Heterogeneous Cluster Distribution

The above considerations regarding the cluster shape factor and the monomer flux make it possible to discuss more fully the relaxation

time to approach the steady-state cluster distribution for heterogeneous nucleation from the solution phase. It can be shown from the definition of the cluster shape factor that

$$G^*(x^*) = \Delta G_s^* + ax^* + b\Phi^{1/3}x^{*2/3} \qquad \text{(I-44)}$$

where ΔG_s^* is the statistical mechanical contribution to the free energy of formation of the heterogeneous cluster and a and b are constants having their values given by equations (I-15) and (I-16) if an isotropic cluster of flattened hemispherical symmetry is assumed.

Substituting $\Delta G^*(x^*)$ and $D^*(x_c^*)$ into equation (I-37), the following expression of τ_1^* can be derived for heterogeneous nucleation from a solution system corresponding to the situations for the flux of the monomers:

Volume-diffusion-controlled mechanism:

$$\ell n\ \tau_1^* = \ell n\ K_2 + \frac{\Delta U}{kT} + B\ \gamma_a^{\ 2}\ \ell n^{-1}(a_1/a_o) \qquad \text{(I-45)}$$

where

$$K_2 = \frac{\lambda h\gamma(2-\mathrm{Cos}\theta - \mathrm{Cos}^2\theta)}{A_2k^2T^2\ \ell n^2(a_1/a_o)} \qquad \text{(I-46)}$$

Surface-diffusion-controlled mechanism:

$$\ell n\ \tau_1^* = \ell n\ K_3 + \frac{\Delta U_D}{kT} + B\gamma^2_{\ a}\ \ell n^{-1}(a_1/a_o) \qquad \text{(I-47)}$$

where

$$K_3 = \frac{8\ \lambda\Omega\gamma^2\Phi}{A_2k^2T^2n_s\ \bar{\delta}\ \bar{\omega}\ \mathrm{Sin}\theta\ \ell n^3(a_1/a_o)} \qquad \text{(I-48)}$$

Similar expressions can also be derived when both the volume diffusion

mechanism and the surface diffusion mechanism for the flux of monomers are considered simultaneously.

It should be noted that the binding energy for two-dimensional nucleation takes different values for different foreign surfaces if the surface diffusion mechanism is to apply predominantly for the heterogeneous nucleation process. This characteristic feature is very useful for verification of the mechanism of heterogeneous nucleation from an aqueous solution system through the relaxation-time approach.

Relaxation Time to Achieve the Occurrence of the Critical Heterogeneous Cluster

From the relaxation-time approach for evaluating the occurrence of the critical cluster for a homogeneous nucleation process, it is apparent that a similar approach should apply for a heterogeneous system. The equilibrium concentration of the critical heterogeneous cluster is given by the relation[74]

$$N^*(x_c^*) = N_1^* \exp\left[- \frac{\Delta G^*(x_c^*)}{kT} \right] \qquad (I\text{-}49)$$

where N_1^* is the equilibrium concentration of the monomer adsorbed on a foreign surface and $\Delta G^*(x_c^*)$ the free energy of formation of the critical heterogeneous cluster as defined previously. In this case, the probability of finding a heterogeneous cluster to be of the critical size becomes

$$P^*(x_c^*) = \frac{N^*(x_c^*)}{N_1^*} = \exp\left[- \frac{\Delta G^*(x_c^*)}{kT} \right] \qquad (I\text{-}50)$$

The steady-state heterogeneous nucleation rate is defined by

$$J^* = D^*(x_c^*)\, N^*(x_c^*)$$

$$= A_1^* \exp\left[-\frac{\Delta G^*(x_c^*)}{kT}\right] \qquad \text{(I-51)}$$

where A_1^* is a pre-exponential factor.

From the definition of the heterogeneous nucleation rate, the expression for the relaxation time to achieve the occurrence of a critical heterogeneous cluster in a solution system is

$$\tau_2^* = \frac{1}{A_1^* S \exp\left[-\frac{\Delta G^*(x_c^*)}{kT}\right]} \qquad \text{(I-52)}$$

or

$$\ell n\, \tau_2^* = \frac{\Delta G_s^*}{kT} - \ell n\,(A_1^* S) + \frac{16\pi\gamma^3 M^2 \Phi}{3\rho^2 N^2 k^3 T^3}\, \ell n^{-2}(a_1/a_o) \qquad \text{(I-53)}$$

where S is the total foreign surface area immersed within a solution droplet. It should be noted that τ_2^*, defined as the relaxation time to achieve a critical heterogeneous cluster within a solution system, depends upon the cluster shape factor as well as the supersaturation condition. Thus the relaxation time τ_2^* could be small in comparison with the relaxation time τ_1^* in some systems, depending on the cluster shape factor.

CHAPTER III

EXPERIMENTAL INVESTIGATIONS

The droplet techniques employed in this study were devised to fulfill the basic requirement for a nucleation investigation. Aqueous solution droplets of sodium chloride in the micrometer(μm) size range were dispersed into air or suspended upon selected foreign surfaces. Undesired effects which might be caused by impurities were therefore largely eliminated. The temperature and the pressure of the system were held constant during an experiment. Equilibrium humidity was the controlling parameter of the system. Experiments to verify the relationships between relaxation times and supersaturation conditions for the nucleation process described in previous chapters could then be performed for alkali chlorides.

Airborne Droplet System

The arrangement of the experimental apparatus for the airborne droplet system is given diagrammatically in Figure 1. Aerosols of sodium chloride were generated by atomizing a 0.1 per cent aqueous solution with a DeVilbiss ultrasonic nebulizer, Model 880. A glass trap was employed to remove the larger droplets. The aerosol was next diluted with an air stream of pre-conditioned humidity to the desired aerosol concentration. The equilibrium humidity condition of the resultant aerosol was determined and controlled by regulating flow rates. Since the humidity of the dilution air was lower than the

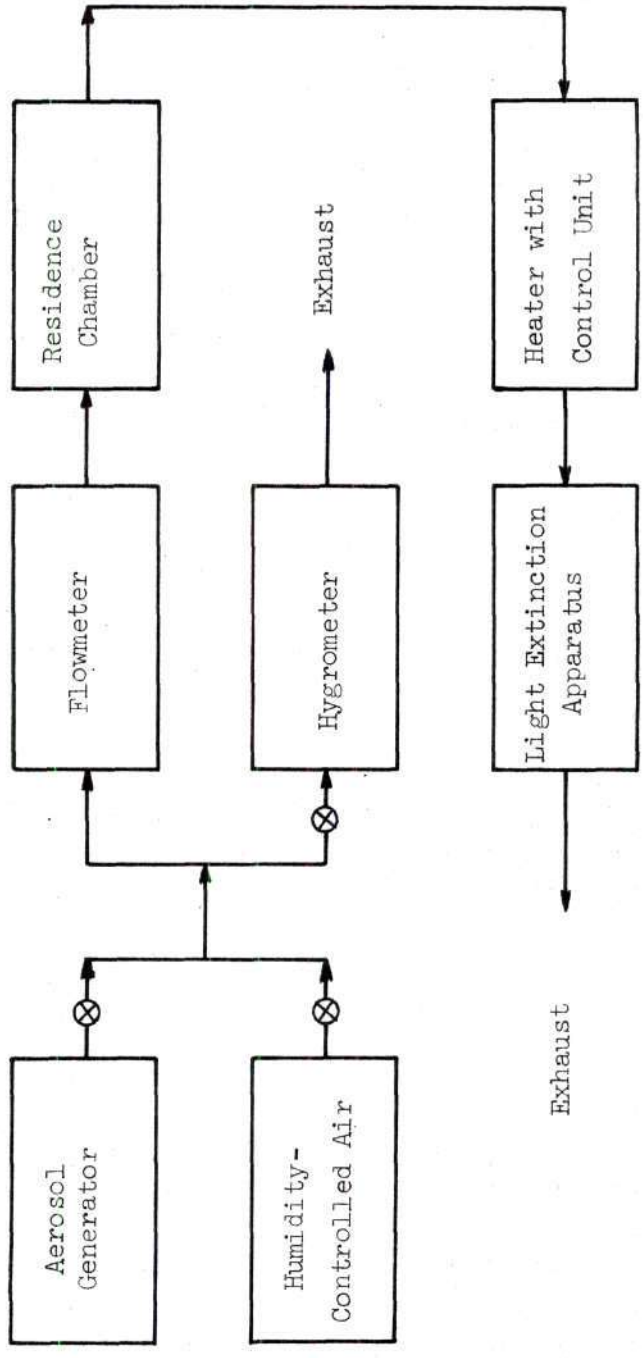

Figure 1. Diagram of the Airborne Droplet Measurement Apparatus.

resultant humidity of the mixture, the dilution air was cooled before mixing to prevent nucleation which could be caused by an inhomogeneity of humidity at the mixing zone. The relative humidity of the resultant aerosol was measured by a Cambridge thermoelectric hygrometer, Model 880.

In order to hold the aerosol for various periods of time after the resultant humidity condition was achieved, two aerosol residence chambers were constructed. A glass chamber with variable volume permitted holdups of up to four minutes with a continuous laminar flow of aerosol of 4 liters/min. A stainless steel chamber of 80-liter volume was employed for longer residence times both in the continuous flow and aging experiments.

The aerosol from the residence chamber was monitored with a system consisting of a resistance heater and a light extinction apparatus. The heating was controlled by a foot switch. With the heater the aerosol could be heated a few degree above room temperature to cause it to contain only dry crystals of sodium chloride. The aerosol was cooled to room temperature upon entering into the light extinction measurement apparatus. The light extinction apparatus consisted of a 4 feet long vertical glass tube of 13/16 inch inside diameter; it had a light source at one end and a light detector at the other. The light detector was connected to a recorder. Differences in the reading of light intensity with and without the tubing heater on indicated whether or not the aerosol contained solution droplets. The tubing heater needed to be on only about 5 seconds before the light signal indicated the aerosol was completely nucleated to dry crystals.

Two methods were employed to determine induction times for the aerosol at corresponding equilibrium humidity conditions: a continuous flow and an aging method. For the continuous flow method the induction time was pre-determined by adjusting the volume of the residence chamber. The aerosol was monitored continuously with the light extinction apparatus. Different humidity conditions for the aerosol were tested for each residence time, giving a continuous curve representing the relation between the steady-state light intensity and the corresponding humidity. The highest humidity at which all droplets became dry crystals was taken as the induction time; it was equivalent to the residence time in this case. The aging method was employed for induction times greater than 1800 seconds. The stainless steel residence chamber was first filled with the aerosol at a pre-determined humidity. Samples of aerosol was taken periodically for examination with the light extinction apparatus by introducing an air stream of the same humidity into the chamber. The resulting light intensity readings were compared with and without applying the tubing heater. The induction time at the corresponding humidity was taken as the time elapsing to the midpoint of the last test at which droplets were detected and the next test when no droplets were detected. Induction times of up to about 60,000 seconds were obtained for different humidities in this manner.

Particles of dry sodium chloride crystals were sampled by a thermal precipitator. Their size was determined to be 0.5 ± 0.2 μm in diameter from photographs made with an electron microscope. The mass concentration of the aerosol was determined by a particle mass

monitor, Model 3205A of Thermo Systems, Inc., to be about 1.5×10^{-5} gm/liter. The number concentration of the aerosol was about 10^5 particles/cm^3.

Surface-Suspended Droplet System

The simple apparatus devised for this portion of the study was similar to those employed previously for study of the phase transition behavior of condensation nuclei.[76,77,78] An aqueous solution of sodium chloride was atomized and a few of the droplets were captured on the surface of interest. This sample was then placed in a chamber mounted on the stage of an optical microscope. Two filtered air streams, one relatively dry and the other made more humid by bubbling through a water column, were proportionally mixed to yield a stream of the desired humidity. One of the humidity-controlled air streams was adjusted to a relative humidity of about 80% to grow the crystals into solution droplets. The other was maintained at a lower relative humidity to nucleate the droplets into dry crystals. The dew point temperature of the latter stream was continuously monitored by a Cambridge thermoelectric hygrometer, Model 880. The dew point temperature of the mixed air stream could normally be maintained within $\pm 0.1^{\circ}F$, without further adjustment once desired conditions were established. Both streams were held at room temperature which was very nearly constant during an experiment. A glass beaker containing $CuSO_4$ solution was placed between the microscopic illuminator and the sample to remove most of the heat in the light. The microscopic illuminator was set at the lowest usable intensity and was turned on only when a quick check

was required. Temperature change caused by the illumination was therefore negligible during the experiment.

To initiate a test, the air stream of higher humidity was introduced into the chamber until all crystals completely dissolved. The flow was then shifted to the air stream of pre-determined lower humidity at a flow rate of 0.5 liter/min. The droplets evaporated very quickly to reach an equilibrium condition. Induction time recording was started when the equilibrium size of the droplets was observed. Induction time was considered ended when a crystal first appeared within a droplet. The droplets selected for study were always less than 50 μm in diameter. The same droplets were observed repeatedly to obtain the data at various humidity conditions for a particular surface. In general, it was noted that induction times for different droplets at the same humidity condition fell within a narrow range of values.

Various surfaces were employed. Smooth and uniform threads of spider web and fiber glass having diameters of about 3 and 10 μm, respectively, were mounted on a steel wire frame. They were washed in an ultrasonic water bath to remove soluble impurities before use. Clean, flat microscope slides coated with thin films of Dow Corning 200 silicone fluid and with Apiezon grease were also used.

CHAPTER IV

RESULTS AND DISCUSSIONS

Homogeneous Nucleation from Supersaturated Solutions

Several induction time measurements were carried out at different equilibrium humidity conditions at room temperature ($23^{o}C$) with the airborne droplet system. The results of these experiments are summarized in Table 1.

According to equation (I-33), the induction time for a homogeneous nucleation process can be interpreted in terms of supersaturation or of the solute activity of the system. Thus the dependence of solution concentration on equilibrium humidity was vitally important in this study. The properties of supersaturated solutions of some of the alkali chlorides have been reported.[79] Corresponding values of solution concentration and of $\ln^{-2}(a_1/a_o)$ are also presented in Table 1.

Experimental values of the induction time were plotted on a logarithmic grid against $\ln^{-2}(a_1/a_o)$; these data are presented in Figure 2. The kinetic constant was evaluated from the intersection of the straight line at $\ln^{-2}(a_1/a_o) = 0$, while the cluster-solution interfacial free energy was calculated from the slope of the straight line. The kinetic constant and the interfacial free energy obtained are 10^{48} cm^{-3} sec^{-1} and 115.9 erg cm^{-2}, respectively, for homogeneous nucleation from aqueous sodium chloride solutions.

Table 1. Homogeneous Nucleation Data for Airborne Aqueous Sodium Chloride Solution Droplets.

Induction Time (sec)	Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-2}(a_1/a_o)$
6	44.4	13.90	0.105
60	44.8	13.74	0.108
240	45.0	13.68	0.109
1,200	45.2	13.60	0.111
1,800	45.5	13.54	0.112
10,500	45.4	13.54	0.112
22,500	45.9	13.37	0.115
34,200	46.6	13.15	0.120
63,000	48.0	12.66	0.131

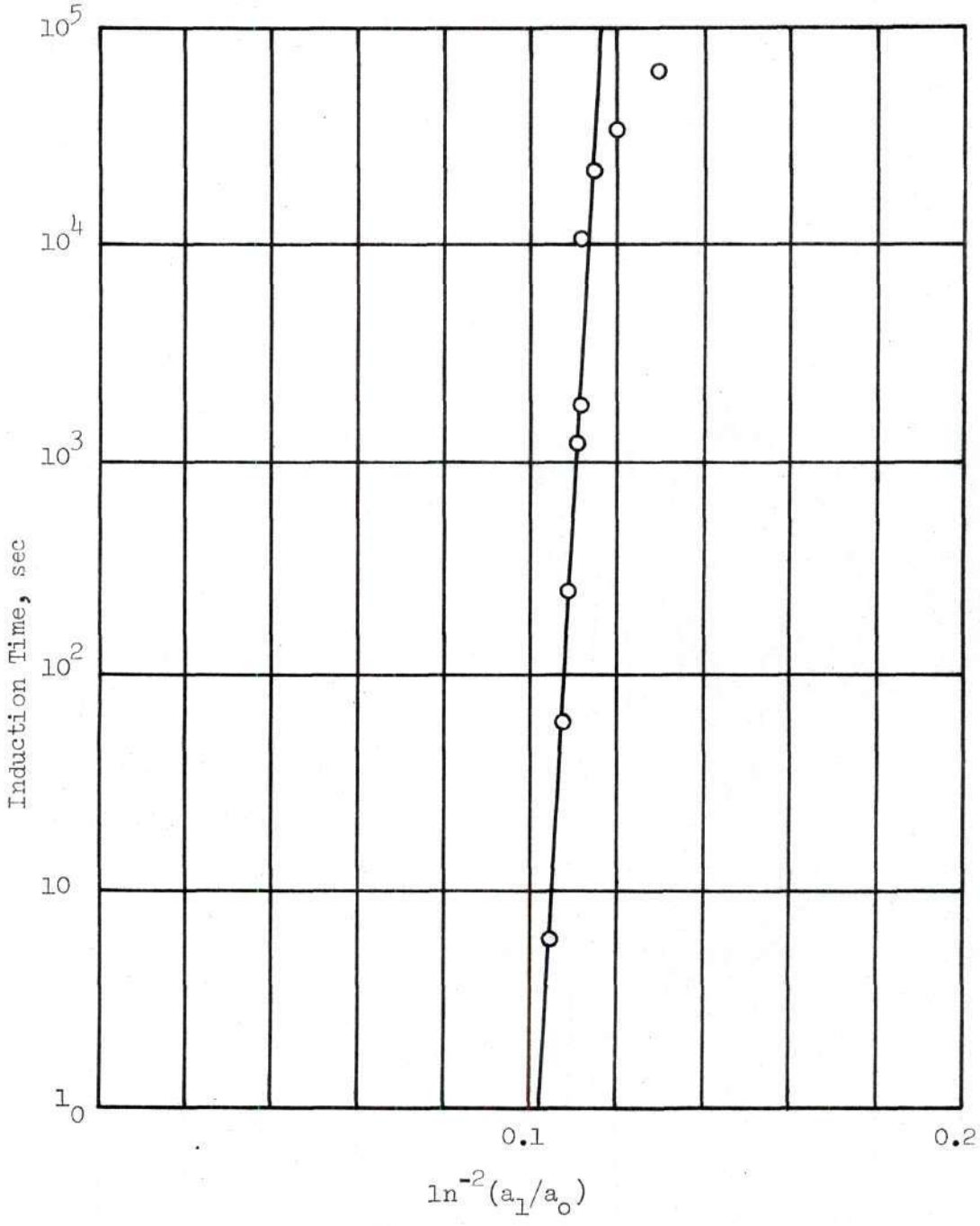

Figure 2. Induction Time of Airborne Aqueous Sodium Chloride Droplets as a Function of $\ln^{-2}(a_1/a_o)$.

The kinetic constant, as predicted by classical theory for the homogeneous nucleation of crystals from condensed systems, is 10^{33} cm^{-3} sec^{-1}.[16] However, by considering the statistical mechanical contributions to the free energy of formation of the critical cluster, Lothe and Pound[20] were able to show that a factor of about 10^{12} should be added in this case. Accordingly, a surprisingly good agreement between the present experimental result and the new theory is obtained. It is to be noted that, similarly, larger kinetic constants have been obtained for liquids such as mercury,[36], water,[37] and polyethylene.[38]

Due to the uncertainty of the crystal-solvent interaction, theoretical prediction of the interfacial free energy for the aqueous sodium chloride system is not presently feasible.[80] Normally the interfacial free energy of a crystal-solvent system would be expected to yield values of 15 to 500 erg cm^{-2}.[81] Since the interaction between a strong interacting, high-lattice-energy crystal and a strong polar solvent leads to a lower value of the interfacial free energy, the experimental value obtained seems very reasonable.

The size and the free energy of formation of the critical homogeneous cluster of sodium chloride at various supersaturations were calculated by substituting the experimental value of the interfacial free energy into equations (I-14), (I-15), (I-16) and (I-18). These results are presented in Table 2. It should be noted that a critical homogeneous cluster generally consists of less than 100 molecules at normal nucleation conditions.

Many attempts have been made in the past to study the homogeneous nucleation of crystals from aqueous solution of soluble salts by

Table 2. Properties of Critical Clusters of Sodium Chloride in Aqueous Solutions.

Solution Concentration (molality)	x_c (No. of Molecules)	$\Delta G(x_c)$ (10^{-12} erg)	$-\frac{\Delta G(x_c) - \Delta G_s}{2.303\ kT}$
10.00	240	9.230	98.08
10.50	177	7.529	80.00
11.00	137	6.348	67.45
11.50	110	5.492	58.36
12.00	90	4.807	51.08
12.50	76	4.296	45.65
13.00	65	3.879	41.22
13.50	57	3.542	37.64
14.00	51	3.274	34.79
14.50	46	3.050	32.41
15.00	42	2.863	30.42

employing the droplet technique. White and Frost[39] were the first to apply the technique by studying the nucleation of aqueous ammonium nitrate solutions. Melia and Moffitt[40] studied the nucleation kinetics of ammonium chloride and bromide and concluded that the kinetic constants were in the range 10 to 10^4 cm^{-3} sec^{-1}, which seems to be unreasonably low. More recently, similar results were obtained by Velazquez and Hileman[42] for aqueous $K_2Cr_2O_7$ and several other systems. Usually the solution droplets were dispersed into another suspending medium as droplets of 0.1 mm or larger in diameter. Explanation for this discrepancy between the experimental and calculated values may reside in the effect of the foreign surface on nucleation.

Experimental determination of the kinetic constants by precipitation has also been used extensively.[10,71,81-84] Rapid mixing of two stable solutions, one containing the cation and the other the anion of the precipitating substance, can establish a highly supersaturated condition. The induction time and the resulted particulate number concentration are measured as a function of supersaturation. Although interfacial free energies calculated from this type of experiment are of a reasonable order of magnitude,[10,85] the kinetic constants are about 10^{10} less than predicted by classical theory.[82] The effects of walls and of turbulence may alter the nucleation process. Impurity particles may also play a part in the results.

In comparison with other methods for studying homogeneous nucleation, the airborne droplet technique has advantages which may be summarized as follows:

1. Droplets of very small size are dispersed into a gas

instead of into a liquid suspending medium, eliminating the effects of foreign surfaces.

2. The supersaturation of the droplets can be created and controlled uniformly at constant temperature.

3. Induction time is determined by a simple operating procedure. No tedious and inaccurate counting of the frequency of crystallization under magnification is required.

4. Induction time measurements provide information over a wide range of supersaturation conditions. The kinetic constant and cluster-solution interfacial free energy can be calculated independently.

There are also disadvantages of the airborne droplet technique. Only certain substances with suitable solubility and hygroscopicity can be studied. A study of homogeneous nucleation using an aqueous potassium iodide system has proved that accurate values for the properties of the supersaturated solution must also be available.[86]

Several improvements are, of course, possible for the experimental investigation. The data would be more reliable if the size and the number concentration of the solution droplets were more closely adjusted so that the error caused by sedimentation and coagulation could be minimized. This becomes more important if long induction time measurements were desired. A more sophisticated light extinction apparatus than employed here would have been helpful for better determination of the induction time.

Heterogeneous Nucleation from Supersaturated Solutions

Induction time measurements of aqueous sodium chloride solution droplets nucleating on selected foreign surfaces at different equilibrium

humidity conditions were performed at room temperature. The surfaces employed were Dow Corning 200 silicone fluid, Apiezon grease, fiber-glass thread and spider silk. Tables 3, 4, 5 and 6 summarize the experimental results.

The dependence of induction time on solution supersaturation was correlated by plotting experimental values of the induction time on a logarithmic grid against $\ln^{-1}(a_1/a_o)$. These results are presented in Figure 3. According to equations (I-45) and (I-47) the linear relationships suggest that, for the heterogeneous nucleation of crystals from aqueous solutions, the induction time is governed by the relaxation time to approach the steady-state probability distribution of the heterogeneous cluster. It can also be deduced that a two-dimensional growth mechanism for the crystalline cluster, as proposed by equation (I-20), prevails.

It has been suggested that such experimental data can also be correlated by plotting the induction time in the same manner against $\ln^{-2}(a_1/a_o)$.[86] This is predicated on the idea that the induction time for heterogeneous nucleation should show a dependence on supersaturation similar to the homogeneous case. The induction time is assumed to be governed by the relaxation time to achieve the occurrence of a critical heterogeneous cluster. Although the data for droplets nucleating on Dow Corning 200 silicone fluid and Apiezon grease give generally linear plots, significant deviations occur for the fiber-glass thread and spider silk cases, the deviations becoming more apparent as the induction times increase. This entire idea is proved erroneous by evaluating cluster shape factors according to Equation (I-53). Since

Table 3. Heterogeneous Nucleation Data for Aqueous Sodium Chloride Droplets on Glass Surface Coated with Dow Corning 200 Silicone Fluid.

Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-1}(a_1/a_o)$	Induction Time (sec)
43.5	14.25	0.316	7
43.8	14.12	0.319	8
46.6	13.15	0.346	22
47.2	12.94	0.354	30
47.6	12.80	0.358	37
48.0	12.66	0.363	56
48.2	12.60	0.366	54
48.8	12.42	0.373	100
49.5	12.21	0.381	170
50.6	11.86	0.398	950
51.3	11.68	0.408	6,750

Table 4. Heterogeneous Nucleation Data for Aqueous Sodium Chloride Droplets on Glass Surface Coated with Apiezon Grease

Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-1}(a_1/a_o)$	Induction Time (sec)
46.2	13.25	0.344	7
49.0	12.35	0.376	12
49.6	12.22	0.381	22
50.6	11.90	0.396	70
51.1	11.72	0.406	320
52.0	11.47	0.420	1,400
53.6	11.02	0.447	8,200

Table 5. Heterogeneous Nucleation Data for Aqueous Sodium Chloride Droplets on Fiber Glass Thread

Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-1}(a_1/a_o)$	Induction Time (sec)
46.3	13.24	0.344	3
49.0	12.35	0.376	6
50.3	11.97	0.392	8
54.0	10.92	0.456	16
55.7	10.48	0.491	23
56.2	10.35	0.504	27
58.5	9.80	0.565	70
61.0	9.20	0.670	350
64.3	8.45	0.850	2,500
65.8	8.14	0.970	7,500

Table 6. Heterogeneous Nucleation Data for Aqueous Sodium Chloride Droplets on Spider Silk

Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-1}(a_1/a_o)$	Induction Time (sec)
47.6	12.80	0.358	2.4
48.4	12.54	0.367	2.9
48.6	12.47	0.371	3.0
52.1	11.44	0.422	5.5
52.8	11.24	0.434	6.5
54.3	10.84	0.462	9.8
56.0	10.40	0.499	12.0
57.0	10.16	0.523	16.5
57.6	10.01	0.540	20.0
58.1	9.90	0.553	21.5
58.4	9.82	0.564	23
61.2	9.17	0.667	42
63.0	8.75	0.758	68
63.9	8.54	0.818	110
64.2	8.45	0.848	135
64.8	8.33	0.891	200
65.4	8.20	0.943	260
66.4	7.98	1.058	450
66.8	7.90	1.100	540
68.1	7.62	1.291	1950
68.4	7.57	1.338	2650
68.9	7.48	1.427	4600
69.2	7.40	1.512	7800

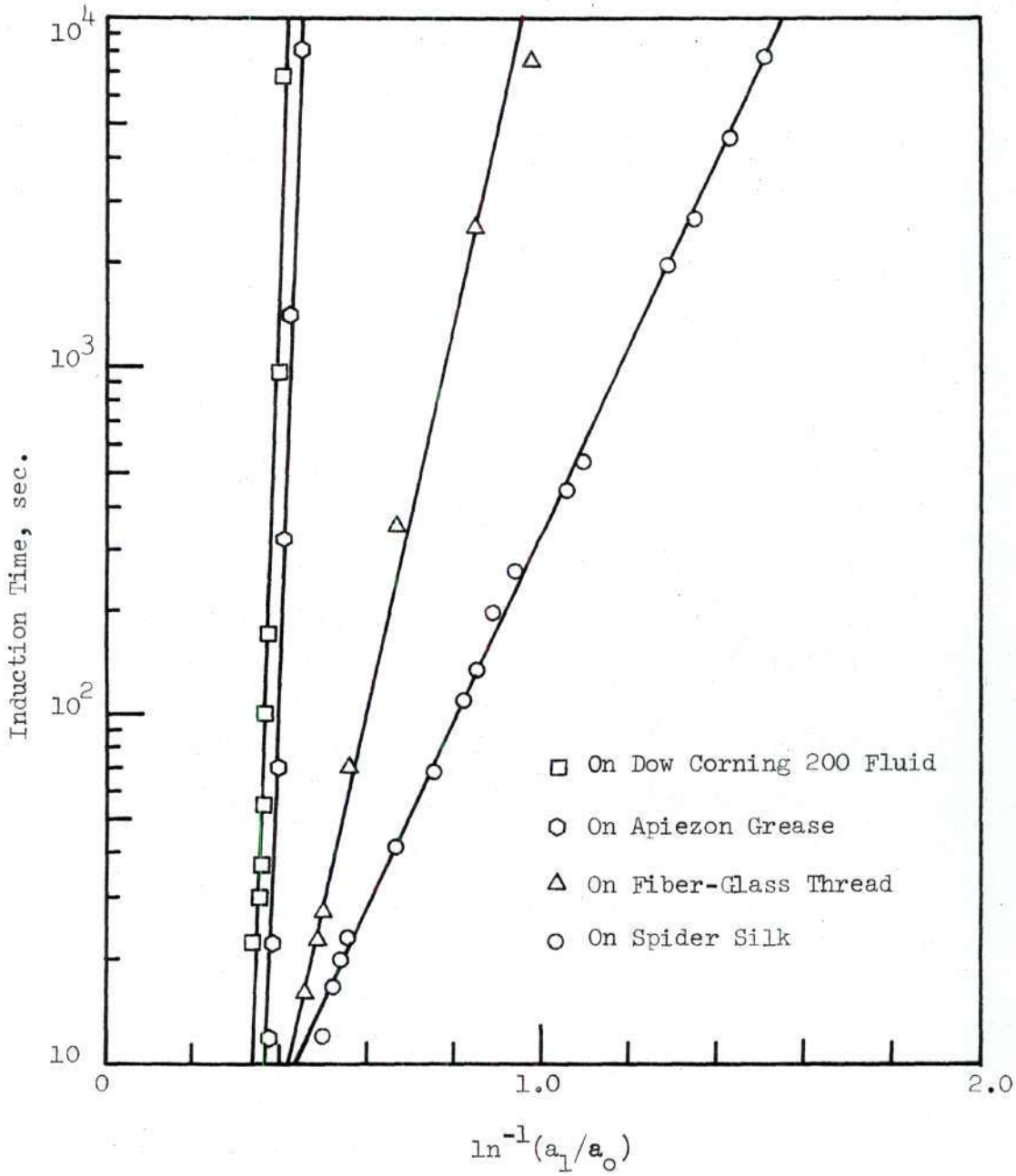

Figure 3. Induction Time of Aqueous Sodium Chloride Droplets on Various Surfaces as a Function of $\ln^{-1}(a_1/a_o)$.

the theoretical kinetic constant for heterogeneous nucleation generally has a value of about 10^{22} cm^{-2} sec^{-1},[87] estimated values for the relaxation time τ_2^* would be very small in comparison with actual induction times measured at the same supersaturation conditions.

A clearer proof of the present correlation can also be obtained from the nucleation frequency observations. Supersaturated solution droplets on surfaces were observed to nucleate within a rather discrete time interval. Droplet size did not seem to influence the induction time. These pieces of evidence fit the probabilistic nature of nonsteady-state nucleation[88,89] and, therefore, lead to the conclusion that the relaxation time for approach to the steady-state probability distribution is the determining factor for heterogeneous nucleation processes in aqueous solutions.

In Figure 3 it is evident that the straight lines obtained for different foreign surfaces have different slopes. This implies different binding energies for two-dimensional nucleation on the clustering mechanism. According to equation (I-47), a surface diffusion process predominates for heterogeneous nucleation of crystals from solutions.

Effects of Soluble Impurity on Nucleation

An effect of soluble impurities on the crystallization of supersaturated salt solutions has long been recognized.[11,46] It appears that impurities can affect the process in many ways. Trace quantities of specific impurities may drastically reduce the crystal growth rate. The supersaturation required for nucleation as well as the

final crystal habit may significantly be changed. Active impurities may coprecipitate with the salt, but the distribution of the impurity between the crystallizing salt and the solution appears to vary peculiarly.

Lead ions were found to be most active in the case of alkali halides. A small quantity of lead chloride significantly reduces the rate of crystal growth of potassium chloride and sodium chloride.[90-97] Supersaturation at the instant of potassium chloride solution crystallization was found to vary with the concentration of lead ions,[98] these data being obtained by cooling an aqueous potassium chloride solution. The solution was stirred during the experiment and the crystallization points were detected by a calorimetric technique. The effect of stirring is not known, so the data can be viewed only as an indication of the role of lead ions on nucleation by comparison with solutions having different lead concentrations.

The effects of lead ions on the nucleation of crystals from aqueous sodium chloride solutions were studied in the present research using both the airborne droplet technique and the surface-suspended droplets system. Induction times at different supersaturation conditions were measured. Solution droplets with 100 ppm (mole $PbCl_2$/mole NaCl) lead ions present were studied first on the spider silk. The results are presented in Table 7. The data with and without lead contamination as a function of $\ln^{-1}(a_1/a_o)$ are also presented in Figure 4 for comparison. It is seen that the lead ions change the binding energy for two-dimensional nucleation as well as the flux of the monomers for clustering.

The possible effects of impurities have been summarized by Hirth and Pound.[6] Impurity adsorption is likely to lower ΔG_{des} for

Table 7. Heterogeneous Nucleation Data for Aqueous Sodium Chloride Droplets with 100 PPM Lead Chloride on Spider Silk.

Relative Humidity (%)	Solution Concentration (molality)	$\ln^{-1}(a_1/a_o)$	Induction Time (sec)
46.6	13.15	0.346	6
51.3	11.67	0.408	11
54.6	10.78	0.465	21
57.5	10.04	0.536	43
59.3	9.62	0.591	56
59.5	9.56	0.600	68
61.4	9.12	0.674	120
64.0	8.50	0.833	520
65.2	8.25	0.921	840
65.4	8.20	0.945	1,100
66.5	8.00	1.040	6,400

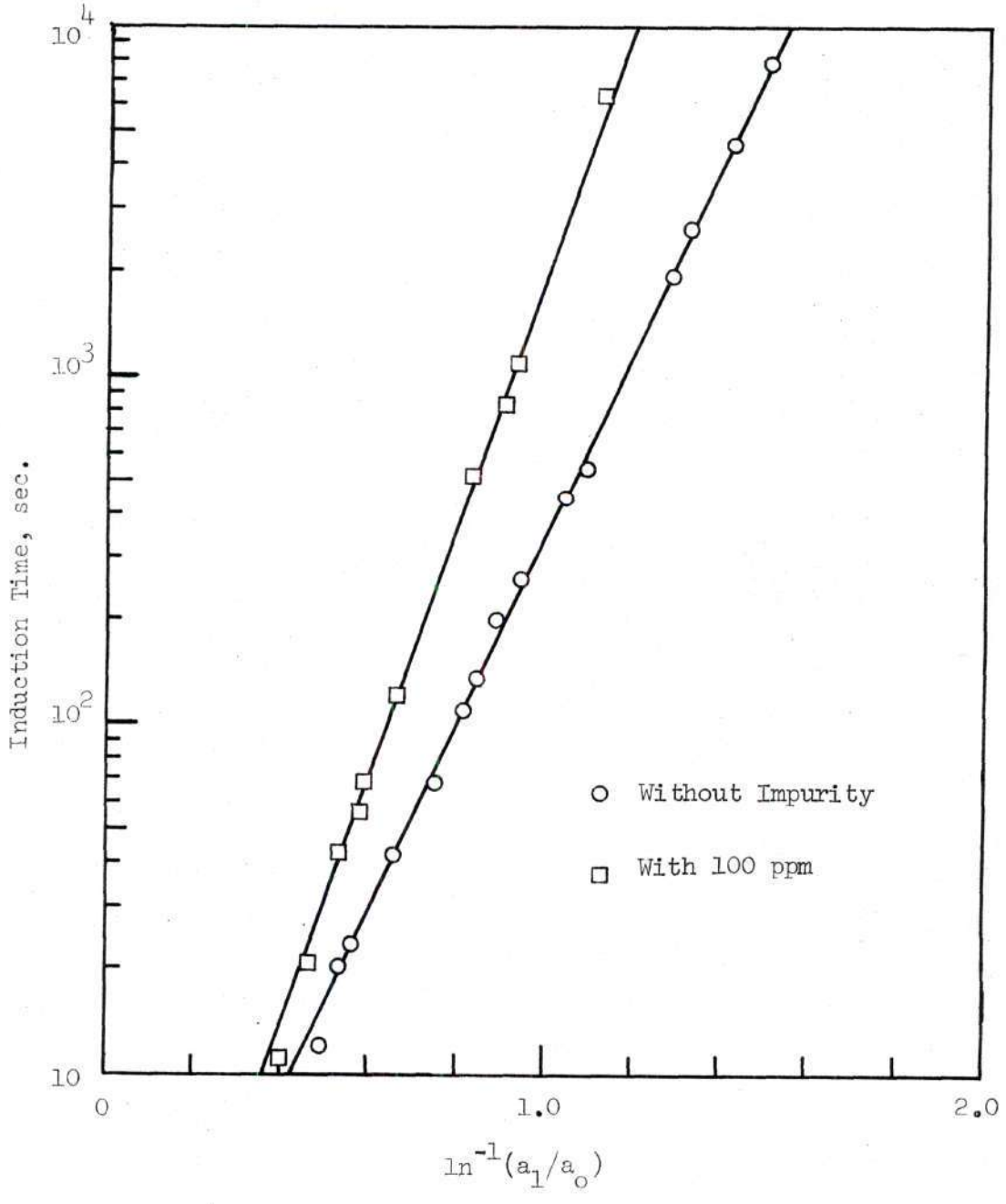

Figure 4. Effect of Lead Chloride on the Induction Time of Aqueous Sodium Chloride Droplets on Spider Silk.

the monomer and, hence, decrease the monomer concentration on the foreign surface. Therefore this reduces the monomer flux to the cluster. It is also believed that an impurity may decrease solution-surface and cluster-solution interfacial free energies and change the binding energy for two-dimensional nucleation. Present experimental results confirm these possibilities, and indicate that the binding energy for two-dimensional nucleation is increased in the lead contaminated aqueous sodium chloride solution situation.

A completely different hypothesis has been suggested by Glasner and Skurnik.[96] It is based on the formation of "heterogeneous clusters" in the supersaturated solution centered on the ions of the impurity. This controversal hypothesis has caused much confusion recently.[97,99,100] To test it, careful airborne droplet experiments were performed. The results indicated that even with a lead ion concentration of up to 1%, no effect on the nucleation of solution droplets can be detected. It is apparent that the hypothesis cannot be of general validity but may be effective under certain special experimental situations.

CHAPTER V

CONCLUSIONS

Solutions of the Zeldovich-Frenkel equation lead to two relaxation times: the relaxation time to approach a steady-state cluster probability distribution and the relaxation time to achieve the occurrence of a critical cluster. Theory and experimental observation agree that, for nucleation from supersaturated aqueous solutions, the induction time of a homogeneous nucleation process is governed by the latter while the former plays a very important role in heterogeneous nucleation. Relationships between relaxation times and the conditions of supersaturation have been established for various situations. Analysis of the probabilistic aspects of nucleation frequency for small solution droplets also yields valuable information concerning the kinetics of nucleation processes.

Homogeneous nucleation of crystals from supersaturated sodium chloride solutions was studied using a new droplet technique. From a simply derived relationship between relaxation time and the homogeneous nucleation rate, the kinetic constant and the cluster-solution interfacial free energy have been obtained as 10^{48} cm^{-3} sec^{-1} and 115.9 erg cm^{-2}, respectively. These results remove the discrepancy between theory and experiment for homogeneous nucleation from aqueous solutions. The value for the experimental kinetic constant also favors the nucleation theory developed by Lothe and Pound.[20]

The concept of relaxation time provides an effective approach for studying the effects of foreign surfaces and soluable impurities on the nucleation process. From induction time measurements for sodium chloride droplets nucleating on various foreign surfaces, a detailed mechanism which includes adsorption, surface diffusion, and two-dimensional nucleation processes is presented for heterogeneous nucleation of crystals from aqueous solutions. Induction time measurements also indicate Pb^{++} ions poison only heterogeneous clustering in an aqueous sodium chloride solution by changing the binding energy for two-dimensional nucleation.

PART II

CRYSTAL GROWTH

CHAPTER I

INTRODUCTION

General Background

Crystallization from solution, as a unit operation, has been extensively used in the chemical process industry. The study of crystal growth from solution is a problem of major importance to desalination and waste treatment efforts; it is widely encountered industrially in recovery operations, purification procedures, and reclamation processes. The subject is also of considerable interest with important repercussions in life processes through the production and dissolution of bone and teeth materials and pathological stone formation.[10]

Although crystallization has been used extensively in chemical industries for many years, surprisingly little fundamental knowledge of the crystallization process exists. Theoretical work in the field of industrial crystallization from solution has led to several mathematical models by which the behavior of a crystallizer, that is, crystal size distribution and yield, can be predicted.[101-104] However, most of these studies have used assumed or empirical functions to represent the dependence of crystal growth rate on supersaturation. As a consequence, industrial crystallization has been developed largely as an art, guided only by the application of elementary crystallization theory.

Crystals may be grown from vapors, from melts, or from solutions. While methods differ widely, the conditions necessary for growth of a crystal are similar in each case. Under conditions of supersaturation of the mother phase, which may be brought about by supercooling or by concentration beyond the point of thermodynamic equilibrium with the more stable crystal phase, the growth of crystals becomes feasible. It is generally considered that the growth of crystals from solution involves two mechanisms occurring in series: the transport of the solute from the bulk supersaturated solution phase to the crystal surface by a volume diffusion mechanism, and the incorporation of solute into the crystal lattice by a surface mechanism. The rate of crystal growth from solution may therefore, be limited by either or both of these mechanisms. When the solution is quiescent or only slightly agitated, mass transport in the bulk is essentially due to molecular diffusion and, hence, is frequently slower than the surface mechanism and is rate controlling. In the other limiting case where agitation of the bulk solution is sufficiently strong, the mass transport process in the bulk becomes the faster and the growth rate is controlled by the surface mechanism.

The mass transport phenomenon which occurs in the bulk solution phase is similar to that which occurs in many other systems, and may be described by well-established methods.[105,106] Unfortunately, the same cannot be said for the surface mechanism. It is clear that understanding the surface mechanism is important in the overall crystal growth process and not only for those situations in which the surface mechanism is rate controlling. The surface mechanism serves as a

necessary boundary condition for solution of volume diffusion problems even when the process is controlled by the volume diffusion mechanism.

Present knowledge of crystal growth phenomena has largely been developed since 1925. Prior to that time almost all work was related to the interpretation of growth forms, the symmetry, and structural arrangements of crystals.[11] In the last fifty years, theories on crystal growth have been proposed primarily with postulates of mononuclear,[70,107] polynuclear,[82,108-110] or dislocation[66] models for the surface mechanism. To test the theories, most attention was devoted to growth from vapor which was shown less complex than growth from solution. However, no completely satisfactory theory accounting for crystal growth over a wide range of supersaturation conditions was propounded.

Experimental studies of crystal growth from solution are generally not in good agreement with theory according to current research. The experiments are usually performed in stirred systems[12,111] with the growth rate being established by a combination of volume diffusive and surface kinetic processes. Also, the techniques cannot eliminate secondary nucleation at relatively high supersaturation conditions.[111-115] As might be expected, meaningful experimental data on crystal growth rate from solution under controlled conditions of supersaturation are scarce, especially when supersaturation is high. Definitive measurements and a unified theory are therefore badly needed to put crystallization from solution on a sound theoretical bases.

Scope of the Research Effort

Formation of a new crystalline phase from a supersaturated mother phase requires the initial formation of a nucleus. The two-dimensional nucleation theory proposed by Stranski[70] and Kossel[107] involves the simplest and most elegant model for this purpose. Unfortunately, the two-dimensional nucleation theory has been put forward in an erroneous manner. The formation of a two-dimensional nucleus has been viewed in the past intuitively as a steady-state problem. The growth rate of the crystal normal to the crystal face therefore emerged as the product of the steady-state two-dimensional nucleation rate, the surface area of the crystal face, and the step height.[116] The odd result predicted from this theory is that the growth rate is proportional to the surface area which conflicts with experimental findings.[116-118] Furthermore, the binding energy for two-dimensional nucleation was assumed to be of the same order as the crystal-solution interfacial free energy which makes the growth of the crystal impossible at low supersaturation conditions.[116,119-121]

In the present research, the two-dimensional nucleation theory is re-examined theoretically. With the relaxation-time approach of Part I of this thesis, a new relationship between crystal growth rate and supersaturation is developed for crystal growth from solution.

To test the new theory, an experimental investigation of the growth rate of crystals from aqueous sodium chloride solutions at controlled supersaturation conditions was performed using the droplet method. Small crystals entrapped on fine spider-web filaments had water condensed on and evaporated from them by altering the ambient

humidity. The dissolution and reformation of each crystal was followed microscopically while the extent of solution supersaturation was established by humidity equilibria criteria. The droplet method has the advantage that with it wide ranges of supersaturation can be conveniently achieved. The concentration within the droplet can also be assumed homogeneous if the droplet size is small. Using data from experimental measurements of the growth rate of the crystal face together with existing information from the literature, the new relationship between the growth rate and the supersaturation condition was confirmed for aqueous sodium chloride and aluminum potassium sulfate systems at both low and high supersaturations.

CHAPTER II

THEORETICAL CONSIDERATIONS

Crystal growth in a supersaturated solution is governed by at least two processes: the diffusion of solute molecules to the surface of the growing crystal, and solute molecule incorporation into the structure of the crystal lattice. The latter process can be divided into several stages,[6,66] consisting of adsorption of the solute molecule on the surface, diffusion of the adsorbed molecule along the surface, and, finally, incorporation into the crystal lattice.

Crystal growth from solution is a complex problem. Too many theories based on diverse models have emerged during the past fifty years to describe them in detail. Part of the reason for this diversity is attributable to lack of basic knowledge of the crystal surface which makes the existence of different models possible. The more important reason may be, however, that none of the theories has yielded results which can satisfactorily describe or predict the growth rate of crystals as convenient functions of the important independent variables.

Historically, the first theory of crystal growth was developed by Stranski[70] and by Kossel[107] about fifty years ago. It is based on a thermodynamic and kinetic approach for the initial formation of a two-dimensional nucleus on the crystal surface. Later theories included

polynuclear,[82,108-110] dislocation,[66] volume diffusion,[66,122] probabilistic,[123] and many other models.[124-130] The movement of growing steps and computer simulation of the crystal growth process have also been extensively discussed.[131-141] Details of crystal growth theories and their developments have been reviewed extensively by many investigators.[6,106,116,119,142-144] Only two-dimensional nucleation and dislocation theory which relate to surface kinetics will be outlined here. Among the crystal growth theories, the original Stranski-Kossel's two-dimensional nucleation theory seems to be the simplest and yet the most elegant.

Two-Dimensional Nucleation Theory

Mononuclear Model

Stranski[70] and Kossel[107] proposed the first crystal growth theory by considering the growth of a perfect crystal. According to this theory, crystals grow by the addition of layers of molecules to their surfaces. This process consists of the formation of a stable two-dimensional nucleus to initiate a new layer and a series of spreading steps to complete the layer. The original theory assumed that the spreading steps occur much more rapidly than the nucleation steps. This implies that as soon as a critical two-dimensional cluster forms on the crystal surface, a layer is added. With this assumption and viewing the formation of the nucleus on surface as a steady-state process, the growth rate normal to any face of total area S was given as[116]

$$R = J\ S\ d \qquad \text{(II-1)}$$

where J is the steady-state two-dimensional nucleation rate and d the step height. If a disc-shaped two-dimensional nucleus one molecule thick is assumed,[116] the steady-state two-dimensional nucleation rate can be obtained

$$J = K_4 \exp\left[\frac{\pi\gamma_a^2\Omega d}{k^2T^2\ln(1+\sigma)}\right] \qquad \text{(II-2)}$$

where K_4 is the kinetic constant for two-dimensional nucleation; σ the supersaturation equal to $(C-C_o)/C_o$ with C being the bulk solute concentration and C_o the saturation concentration of solute; γ_a the binding energy for two-dimensional nucleation; Ω the volume of a solute molecule; k the Boltzmann constant; and T the absolute temperature.

Polynuclear Model

The polynuclear two-dimensional nucleation model is based on another simple physical picture that differs very considerably from the mononuclear case. It is assumed that the rate at which critical clusters form is rapid relative to the rate at which they spread. Thus the crystal grows by adding several growing nuclei to the surface at the same time. It has led to various growth rate expressions based on different simplifying assumptions.[82,108-110,116] One of these[109] is

$$R = \left(\frac{\pi kT}{h}\right)\left(\frac{\gamma a}{kT}\right)^2\left(\frac{d}{\sigma^2}\right)\exp\left[-\frac{U_E}{kT}\right]\exp\left[-\frac{\pi\gamma_a^2\Omega d}{k^2T^2\ln(1+\sigma)}\right] \qquad \text{(II-3)}$$

where U_E is defined as an activation energy for the entry of a growth unit into the nucleus and h is Planck's constant.

Although the two-dimensional nucleation theory, as described in equations (II-1) and (II-3), are intuitively appealing, there is little experimental evidence that they are applicable. Equation (II-1) predicts that growth rates on crystal faces should be proportional to the area of the face; this dependency appears unrealistic.[116-118] The growth rate of crystals at certain supersaturation conditions; as calculated according to two-dimensional nucleation theory, has been found to be in general agreement with experimental results.[11] However, calculated values of growth rate are much lower than those observed at low supersaturations. The theory has also been criticized on the basis that, if an acceptable value of γ_a is substituted into the growth rate expression, both the mononuclear and polynuclear two-dimensional theories predict the growth will be virtually infinitesimal due to an inadequate surface nucleation rate at supersaturations below about 1 or 2 per cent.[116,119,121] This argument seems to be questionable since γ_a is a poorly understood physical parameter according to present knowledge of the crystal-solution interface. Moreover, equation (II-3) predicts that the growth rate will go through a maximum as the supersaturation is increased, behavior which likewise has not been observed.

Dislocation Theory

In attempting to explain the discrepancies between the Stranski-Kossel theory and experimental observations, the Burton-Cabrera-Frank (BCF) theory[66] was developed. This theory was first used to describe crystal growth from the vapor. The investigators demonstrated that a crystal may show what is called a screw dislocation and thus the spiral-growth theory was developed. New ledges upon which growth can occur are

assumed to be continuously provided from the resulting rotation of the spiral. This surface diffusion model was later extended by Bennema[145-147] to include growth from solution. This theory can be expressed mathematically in the form

$$R = K_5 \left(\frac{\sigma^2}{\sigma_c} \right) \tanh \left(\frac{\sigma_c}{\sigma} \right) \qquad \text{(II-4)}$$

where the constants K_5 and σ_c are characteristic parameters. For low supersaturations, it leads to

$$R = \frac{K_5}{\sigma_c} \sigma^2 \qquad \text{(II-5)}$$

and for high supersaturations to

$$R = K_5 \sigma \qquad \text{(II-6)}$$

The BCF theory generally satisfies results from experimental findings, that is, it predicts a parabolic relation between the growth rate and supersaturation at low supersaturations and a linear dependence at high supersaturations.[116,120,148] However, since experimental investigations under controlled conditions for high supersaturations are very difficult to achieve, molecular diffusion in the bulk becomes a matter of importance at ordinary circumstances. This leads to a linear dependence intuitively for most of the cases. Recent data have indicated that the linear dependence is not always true.[118,149,150] Direct observation of the growing surface in solutions suggests little evidence that the spirals will occur, except in extreme instances when impurities are involved.[151] Furthermore, the derivation of the

theory utilizes more than ten unknown parameters. The theory is truly of dubious value in practice.

Reexamination of Two-Dimensional Nucleation Theory

The most general treatment of nucleation kinetics, according to the Zeldovich-Frenkel equation[44,45] reveals the virtually nonsteady-state character of the nucleation process. In Part I of this thesis it was shown theoretically and experimentally that the nonsteady-state effect plays a major role in the heterogeneous nucleation of crystals from aqueous solutions. The nonsteady-state character becomes more evident when stronger effective foreign surfaces are involved. In these cases, the binding energies for two-dimensional nucleation of the crystal are lower, which makes the required supersaturation for heterogeneous nucleation lower, and causes the relaxation time to approach the steady-state heterogeneous cluster distribution to become a dominent time factor for the initiation of the nucleation.

Crystal growth is a two-dimensional process. The behavior of solute molecules on a crystal surface under supersaturated conditions can also be described by the Zeldovich-Frenkel equation. Therefore the time required to initiate a critical two-dimensional cluster on a crystal surface should include both the relaxation time to approach the steady-state cluster distribution τ_1 and the relaxation time to achieve the occurrence of the critical cluster τ_2. The influence of nonsteady-state effects on the growth of crystals from melts has been examined by Gutzow and Toschev[152] recently. These investigators were able to conclude that the role of nonsteady-state effects becomes significant at high super-coolings, although a completely opposite

opinion does exist.[153] Since crystal growth from aqueous solutions generally requires a much lower supersaturation than that for heterogeneous nucleation, this implies that a much lower binding energy for two-dimensional crystal nucleation is appropriate. Accordingly, it is reasonable to assume that the relaxation time to achieve the occurrence of a two-dimensional critical cluster τ_2 can be ignored in comparison with the duration of the relaxation time to approach the steady-state cluster distribution τ_1. With this assumption, the crystal growth rate normal to a face becomes

$$R = \frac{d}{\tau_1} \qquad \text{(II-7)}$$

where d is the height of the two-dimensional nucleus. τ_1 takes a form similar to that in equation (I-10), that is[49,57]

$$\tau_1 = - \frac{\lambda k T}{D(x_c) \left\{ \frac{d^2 [\Delta G(x)]}{dx^2} \right\}_{x=x_c}} \qquad \text{(II-8)}$$

where x_c represents the number of the molecules in a two-dimensional cluster of critical size; $D(x_c)$ is the flux of the monomers joining the critical cluster; and $\Delta G(x)$ is the Gibbs' free energy of formation of a two-dimensional cluster of size x within the supersaturated solution.

Considering the formation of a disc-shaped cluster on the crystal surface, the free energy of formation of a two-dimensional cluster $\Delta G(x)$, neglecting statistical mechanical contributions, will be

$$\Delta G(x) = -kTx\ln(1+\sigma) + 2(\pi\Omega d)^{1/2}\, \gamma_a\, x^{1/2} \qquad \text{(II-9)}$$

where γ_a is the binding energy for two-dimensional nucleation and Ω the volume of a solute molecule. The value of $\Delta G(x)$ goes through a maximum as the cluster increases to its critical size. Hence the size of the critical cluster may be calculated by letting $[d\,\Delta G(x)/dx]_{x=x_c} = 0$. Thus

$$x_c = \frac{\pi \gamma_a^2 \Omega d}{k^2 T^2 \ln^2 (1+\sigma)} \qquad \text{(II-10)}$$

Here it is assumed the two-dimensional cluster is formed by activated surface diffusion of the monomers onto the crystal surface.[6] The monomers are first adsorbed onto the surface, then they perform a two-dimensional random walk. Some of the monomers encounter a cluster and are incorporated into it before being dispersed into the solution phase again. The surface-diffusion-controlled monomer flux $D(x_c)$ can be expressed in the form[74]

$$D(x_c) = 2\pi\, r_c\, n_s\, \bar{\delta}\, \bar{\omega}\, \beta \exp\left[-\frac{\Delta U_D}{kT}\right] \qquad \text{(II-11)}$$

where r_c is the radius of the critical cluster, n_s the surface concentration of the adsorbed monomers, $\bar{\delta}$ the lattice parameters, $\bar{\omega}$ a vibrational frequency factor, and ΔU_D the activation energy of surface diffusion of the monomer. The factor β expresses the probability of the joining monomer to be incorporated.

Substituting $\Delta G(x)$ and $D(x_c)$ into equation (II-8) and then rearranging equation (II-7), there is obtained

$$R = K_6 \ln^2(1 + \sigma) \qquad \text{(II-12)}$$

where

$$K_6 = \frac{kT\, n_s\, \bar{\delta}\, \bar{\omega}\, \beta}{\lambda\, \gamma_a} \exp\left[- \frac{\Delta U_D}{kT} \right] \qquad \text{(II-13)}$$

Equation (II-12) is a new relationship between the growth rate and the supersaturation of the solution. This new theory predicts a parabolic dependence at low supersaturations since as $\sigma \rightarrow 0$, $\ln(1+\sigma) \rightarrow \sigma$, and at high supersaturations, it predicts a much greater growth rate than the BCF theory.

CHAPTER III

EXPERIMENTAL INVESTIGATIONS

The same simple apparatus and operating conditions were employed for the crystal growth study as used to study the nucleation of aqueous solution droplets on a surface. A few modifications were incorporated to meet the new purpose. A saturated aqueous solution of sodium chloride was atomized and a few droplets were captured on a smooth and uniform thread of clean spider web of about 3 micrometers diameter. The droplets generally converted to crystals before they were placed in the observation chamber since the room air was usually dry enough to induce nucleation. Humid air was then let into the observation chamber, condensing on and dissolving the crystals. Neighboring droplets sometimes joined to form larger droplets. A crystal with a diameter of about 100 micrometers was desired.

The droplet was observed at a magnification of 300, using illumination of as low power as possible. A glass beaker containing water was placed between the microscope illuminator and the observation stage to remove most of the heat in the light; temperature change caused by the illumination was assumed negligible during an experiment. Air flowing at a flow rate of 0.5 liter/min was employed.

The growth of a crystal within the solution droplet was initiated by heterogeneous nucleation at the spider web surface. The induction time for nucleation was predicted according to the experimental results

obtained in Part I of this research for each humidity condition. The growth behavior of the crystal was recorded with a Bolex 16 mm movie camera at a speed of 32 frames per second. Kodak TRI-X reversal film (No. 7278) was used. Growth rates were then determined by viewing the film frame by frame under a microscope. The dimension of the crystallographic face was measured with a filar micrometer eyepiece over the course of each test. Since the dimensions of the crystal within the solution droplet were distorted by refraction, calibration was accomplished by comparing the size of the crystal against that of the spider web.

At high supersaturation conditions, nucleation of several crystals within a single droplet was usually observed. When the supersaturation was relatively low, the duration of the induction time made the procedure described not feasible; growth rate measurements for the aqueous sodium chloride system were achieved at supersaturations between 30 and 70 per cent only.

CHAPTER IV

RESULTS AND DISCUSSIONS

Dimensional measurements of the (100) face of growing sodium chloride crystals as a function of time were carried out for several equilibrium humidity conditions. The results of these measurements are presented in Figure 5.

It is to be noted that during the early stages of the growing process within small aqueous sodium chloride solution droplets the growth proceeded rather uniformly with constant rates. This indicates that the supersaturation within the solution droplets was held homogeneously at a constant value by diffusion of the solute molecules. The decrease of the solute content within the solution phase caused by solute build-up on the crystal surface was well balanced by evaporation of the solvent into the air stream. Crystal growth rates at the pre-determined equilibrium humidity conditions are therefore determined by the rates at this stage. These results are presented in Table 8.

To test the validity of the growth rate equation (Equation II-12), experimental data at low as well as at high supersaturations should be included. The growth rate for as-grown whiskers of the (100) face of sodium chloride has recently been studied[117] at supersaturations from zero to 1.2 per cent. These results with data from the present study are presented in Figure 6 according to the correlation of equation (II-12). Good agreement is evident.

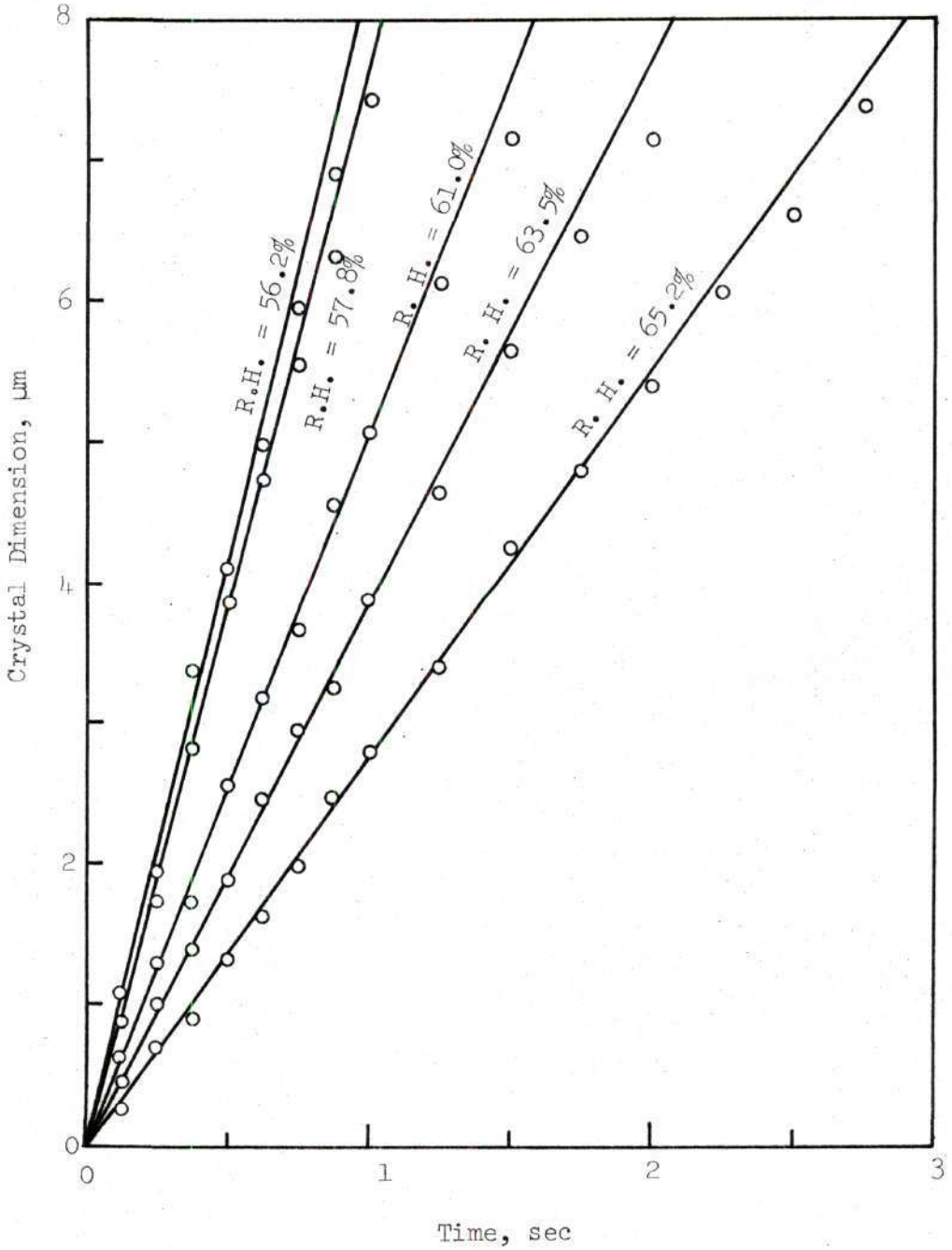

Figure 5. Dimension of Growing Sodium Chloride Crystal as a Function of Time.

Table 8. Crystal Growth Data from Aqueous Sodium Chloride Droplets

Temperature (°F)	Relative Humidity (%)	Solution Concentration* (molality)	$\ln^2(1 + \sigma)$	Growth Rate (μm/sec)
73.5	56.2	10.35	0.271	8.30
74.0	57.8	9.96	0.233	7.75
73.0	61.0	9.20	0.162	5.05
72.8	63.5	8.62	0.114	3.87
73.4	65.2	8.26	0.087	2.73

* Saturation Concentration = 6.15 molality

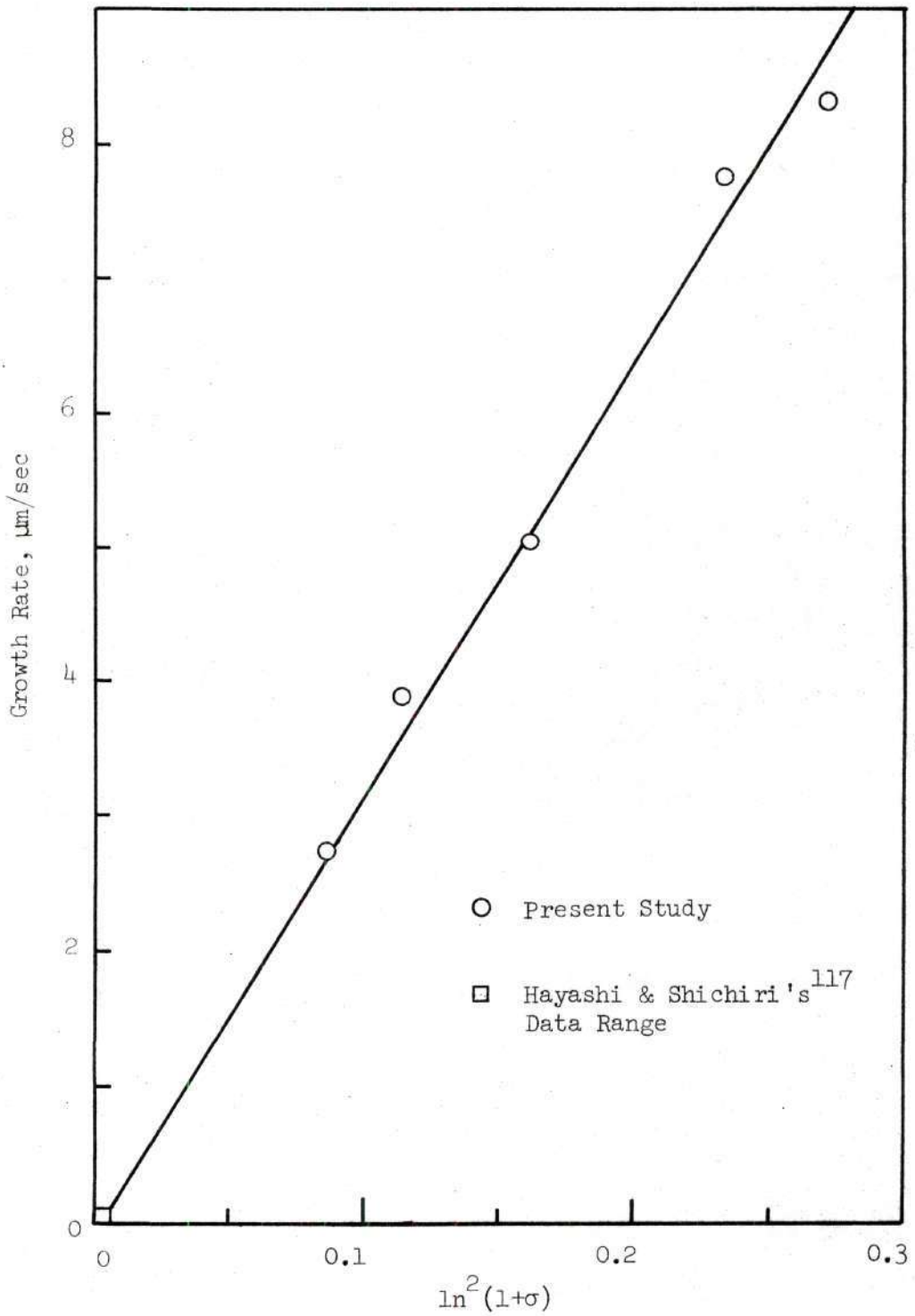

Figure 6. Growth Rate of Sodium Chloride Crystal as a Function of $\ln^2(1+\sigma)$

Quite a number of attempts to derive a kinetic expression, that is, one expressing growth rate as a function of supersaturation, for the growth of crystals from solutions can be found in the technical literature.[142-144] With a few exceptions, parabolic dependence at low supersaturations was found for most of the systems.[143,144,148] Although these results were interpreted in terms of the surface diffusion model of the BCF dislocation theory, they can be used as well as strongly supporting evidence for the new theory. Agreement between the BCF dislocation theory and growth rate measurements at high supersaturations is not so fortuitous, however. Experimental studies on $CaSO_4$,[118] $SrSO_4$,[149] $PbSO_4$,[149] $BaSO_4$,[149,150] and aluminum potassium sulfate (K-Alum)[121] have shown growth rates much higher than the BCF theory predicts.

In the recent articles,[109,110,115,120,121,146,148,154-156] growth of K-Alum crystals over a wide range of supersaturations have been extensively discussed. Bennema[157,158] developed a special weighing procedure to measure accurately the change in mass of a single crystal during growth. The measurements were performed at supersaturations lower than 1.2 per cent at $40^{\circ}C$. Growth rates were found to be linear with supersaturation for values of σ less than 1 per cent. The growth rate deviated, however, from a linear relationship at higher values of supersaturation. Bennema and his coworkers[109] explained this deviation from linear dependence by assuming that both the polynuclear model of the two-dimensional nucleation theory and the surface diffusion model of the BCF theory applied simultaneously. In later studies, Botsaris and Denk[121] were able to extend the growth rate measurements up to 18

per cent supersaturation with a flow crystallizer at 35.1°C under constant flow velocity and supersaturations. They pointed out that the growth rate data show a linear dependence on supersaturation at low supersaturations, but deviate drastically from the linear law at high values of supersaturation. A compound model based on assuming the observed growth rate to be equal to the sum of the growth rate arising from the surface diffusion model of the BCF theory and the mononuclear model of the two-dimensional nucleation theory was then proposed.[115] Although the latter model fitted the experimental data quite well with empirically selected coefficients, this combination of models must be suspect since both cannot coexist because of the assumptions behind each model.[116]

The experimental data for the (111) face obtained by Bennema[158] and by Botsaris and Denk[121] can be used for a critical evaluation of the new theory here. They are plotted according to the proposed correlation, equation (II-12), and presented in Figure 7. Rather good agreement is evident except for the fact that the two experimental sets of data deviate slightly. The fit seems to be quite reasonable, especially so since the experiments of the two investigations were carried out at different temperatures and other conditions.

Most attention in the original crystal growth theories was devoted to growth from the vapor. The mechanism of growth from solution is at present much less well-understood. The rate of crystal growth from the vapor is not limited by mass transfer in the gaseous phase, since such transfer proceeds quite rapidly in the case of a pure gas, at least. In crystal growth from solution, however, if the entire

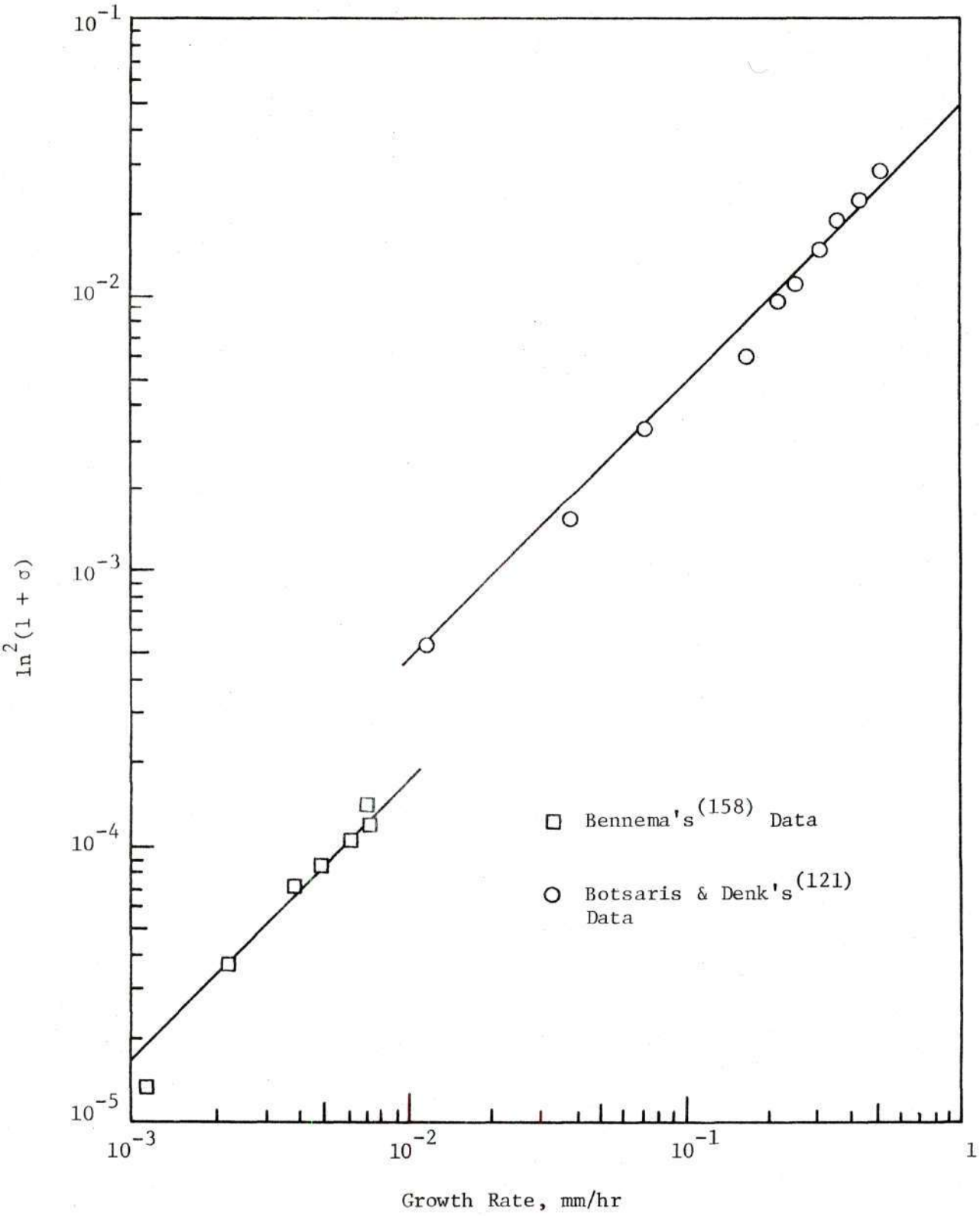

Figure 7. Growth Rate of Aluminum Potassium Sulfate Crystal as a Function of $\ln^2(1 + \sigma)$.

solution is motionless and of sufficiently large volume, the growth rate will be controlled by molecular diffusion within the solution, which is inversely proportional to the thickness of the boundary layer around the crystal surface and directly proportional to the diffusion coefficient. If the solution is stirred, eddy diffusion becomes the mechanism of importance. Even so, a thin layer of liquid remains motionless at the crystal-solution interface, and diffusive transfer of solute through this layer modifies the kinetics of crystal growth.

In typical research on the kinetics of growth from solution, experiments are performed in stirred or flow systems to minimize the uncertainty of the variables. Actually, the rate of growth is thereby established by a combination of diffusive and surface kinetic processes. The effects of stirring have been studied empirically by several investigators.[159-162] Attempts have been made to relate the surface kinetic process and supersaturation to linear and higher order reactions.[12,111] However, any determination of the surface kinetic process from stirred or flow systems can be shown to be impractical according to Brice's approach.[163]

In general, the growth rate R of a crystal face may be approached by a relationship of the form[163]

$$R = K(C_s - C_o)^n \qquad \text{(II-14)}$$

where C_s is the solute concentration at the interface, C_o the saturation concentration in the solution at a fixed temperature, and K and n are constants depending on the system and the growth mechanism. The kinetic constant K is a function of temperature.

Neglecting solute capture by the advancing growth interface, the growth rate on a plane interface may also be written[163]

$$R = V_m \overline{D} \left(\frac{\partial C}{\partial z}\right)_{z=0} = \left[\frac{C_\infty - C_s}{\delta}\right] V_m \overline{D} \qquad \text{(II-15)}$$

where V_m is the molar volume, $\overline{D}$ the diffusion coefficient, $(\partial C/\partial z)_{z=0}$ the concentration gradient normal to the interface, δ the thickness of the boundary layer, and C_∞ the solute concentration in the bulk of the solution outside the boundary layer. By equating equations (II-14) and (II-15) there is obtained

$$\frac{R\delta}{V_m \overline{D}} + (R/K)^{1/n} = C_\infty - C_o \qquad \text{(II-16)}$$

The right hand side of equation (II-16) is now the supersaturation condition normally measured or calculated in crystal growth systems. If the value of n were known, equation (II-16) could be solved to give R as a function of supersaturation. In the absence of this information there are only limiting solutions of interest. These are

$$R = K (C_\infty - C_o)^n \quad \text{for } \delta/\overline{D} \rightarrow 0 \text{ or } K \rightarrow 0 \qquad \text{(II-17)}$$

and

$$R = \frac{V_m \overline{D}}{\delta} (C_\infty - C_o) \quad \text{for } \delta/\overline{D} \rightarrow \infty \text{ or } K \rightarrow \infty \qquad \text{(II-18)}$$

When conditions are such that the stirring is sufficient or that the growth rate is small, equation (II-17) should apply. On the other hand, equation (II-18) prevails.

In the case of crystal growth from aqueous solutions, equation (II-16) must be examined more closely. Values of K are reported[111]

to be in the ranges of 0.1 to 10^5, depending on the aqueous system. Evaluation of δ is complex, but approximate values can be obtained in some cases of interest. In the case of a body immersed in a medium moving with a relative velocity v, the average effective momentum boundary layer thickness can be found by an analysis similar to that of Carlson.[164] The expression reduces to[163]

$$\delta = c\,\overline{D}^{1/3}\,\mu^{1/6}\,(v/L)^{-1/2} \qquad \text{(II-19)}$$

where μ is the kinematic viscosity, L a dimension of the crystal, and c a constant having values in the range of 1 to 10.

A simple calculation shows the boundary layer thickness δ to be between 15 and 150 μm when the typical dimension of the crystal and the relative velocity are taken to be 1 cm and 60 cm/sec, respectively. With such values for the boundary layer thickness, it is concluded from equation (II-16) that volume diffusive effects are always present in growth kinetic studies from solution utilizing stirred or flow systems. The effects become most apparent when the supersaturation is great.

In all reported research, control of supersaturation beyond a few per cent relative supersaturation seems to be impossible due to secondary nuclei formation.[111-116] Comparatively little systematic work on secondary nucleation in agitated systems has been published.[111] Powers[112,113] employed a system in which a sucrose crystal attached to a glass spike was rotated in a supersaturated solution. Even though precautions were taken to ensure that the system was initially free from nuclei, fresh nuclei apparently continued to appear in the

solution. This occurred even at very low supersaturations. Experiments in which a potassium chloride crystal was rotated on a glass spike in a supersaturated solution have been performed by Melia and Moffitt.[114] This study found the number of nuclei in a 800-ml sample (saturated at 50°C) to be about 15,500 at 1°C supercooling and about 36,500 at 2°C supercooling. Although the mechanism of secondary nucleation accompanying agitation is still unknown, its effect on crystal growth from stirred systems is believed to be inevitable and large.

From the work described above it is clear that, in the evaluation of growth kinetics, care must be taken that the surface kinetic process is not masked by volume diffusive effects and that the secondary nucleation process is eliminated completely. Test of theories can only be accomplished after solving two problems which have plagued previous research efforts. These are: (1) control of supersaturation from very low to high values, and (2) elimination of volume diffusive effects and secondary nucleation processes at high as well as low supersaturations.

In previous investigations dealing with the growth of solution droplets in a gaseous medium, it has been implicitly assumed that the solution concentration at each instant of time was constant throughout the droplet.[1,165,166] Aleksandrov, et al.[167] justified this assumption by a numerical calculation and showed that the maximum relative error was within 0.05 per cent for a sodium chloride crystal of 100 micrometers growing at 100 per cent relative humidity conditions. Theoretically, Buikov[168] concluded that, during evaporation or condensation, it may be assumed with little error that the solvent vapor pressure over a droplet surface can be determined by the average bulk solute concentration

for droplets having radii up to 100 micrometers.

During the process of crystal growth within a solution droplet at a fixed humidity condition, mass transfer must occur across the crystal-solution and solution-vapor interfaces. With a droplet size of 100 micrometers or so, it is therefore quite safe to assume a homogeneous solute concentration within the solution phase. It may be noted this assumption is justified by the direct observations of this study.

The technique employed in the present research -- the "droplet" method -- has been shown to meet the stated requirements for crystal growth studies. Ideally high and low supersaturation conditions can be achieved within the droplet, and a wide range of supersaturation can be conveniently controlled by adjusting the ambient humidity. Since the droplet is small and no stirring procedure is involved, volume diffusive effects and secondary nucleation problem can be eliminated.

The apparatus employed in this study can still be improved to yield higher quality data. A more sophisticated magnification and recording system would be helpful for further study on the behavior of the growing surface during crystal growth. If a metal (such as gold) filament were employed, inducing nucleation by electrical current might be very effective in extending growth rate measurements to a much lower supersaturation than is now possible. Nevertheless, the droplet method has the potential to be one of the most effective methods for attacking interesting and complicated crystal growth problems.

CHAPTER V

CONCLUSIONS

Crystal growth from solution is a complex problem. Present theories generally start with postulates of mononuclear, polynuclear, or spiral models. Crystal growth experiments utilizing aqueous solution systems are generally not in good agreement with the theories according to current research. Critical review of these efforts shows that none of the existing theories can account for crystal growth rates at both low and high supersaturations.

Experimental investigations of crystal growth from solutions are also found not to be entirely satisfactory. The experiments usually involve volume diffusive and secondary nucleation processes. It has been shown that meaningful experiments on crystal growth kinetics from solution under controlled conditions of supersaturation are very difficult to achieve with stirred or flow systems, especially when the supersaturation is high.

The droplet method as used in this study has proved to be a very effective approach, however. Since droplet sizes are small, supersaturation within each droplet can be assumed homogeneous. A wide range of supersaturations can be conveniently achieved by adjusting the ambient humidity conditions.

From a most general treatment of nucleation kinetics, the present research shows that nonsteady-state effects should be

considered in two-dimensional nucleation problems. Based on the relaxation-time approach, a new relationship between crystal growth rate and supersaturation for crystal growth from solution has been attained. Using experimental data collected with the droplet method and data from the technical literature, the validity of the new theory (equation II-12) has been demonstrated for aqueous sodium chloride and aluminum potassium sulfate systems at both low and high supersaturation conditions.

RECOMMENDATIONS

Several areas needing further research have become apparent as a result of this approach to the study of nucleation and crystal growth from supersaturated solutions. They are:

1. A study on the frequency of droplets nucleation on a well-defined surface should be made to yield information on the probabilistic nature of the heterogeneous nucleation process. This information would be very helpful in assessing the nonsteady-state character of the process as well as in justifying the validity of solutions of the Zeldovich-Frenkel equation.

2. The effect of lead ions on the growth of sodium chloride crystals from solution should be studied with the droplet method. This would permit a test of the new crystal growth theory established in this research in the impure system.

3. Basic research into the properties of crystal surfaces in solution should be encouraged.

4. The relaxation-time approach should be examined in relation to the basic physical processes in atmospheric phenomena such as cloud seeding and photochemical smog formation.

NOMENCLATURE

A	Pre-exponential factor
a	Constant defined by equation (I-15)
a_0	Activity of solute in a saturated solution
a_1	Activity of solute in a supersaturated solution
B	Constant defined by equation (I-20)
b	Constant defined by equation (I-16)
C	Concentration of Solute
c	Numerical factor defined by equation (II-19)
D	Total monomer flux
D_s	Surface-diffusion-controlled monomer flux
D_v	Volume-diffusion-controlled monomer flux
$\overline{D}$	Volume diffusion coefficient of solute
d	Step height of crystal growth
f	Characteristic function for clustering process
G	Gibbs' free energy for cluster formation
G_s	Cluster free energy due to statistical mechanical contributions
G_v	Free energy per unit volume of solute
h	Planck's constant
J	Steady-state nucleation rate
K	Kinetic constant
k	Boltzmann constant
L	Characteristic dimension of crystal
M	Molecular weight of solute

N	Avogadro number
N_1	Equilibrium concentration of monomer
$N(x_c)$	Equilibrium concentration of critical cluster
n_s	Surface concentration of adsorbed monomer
P	Probability distribution of cluster
p	Probability of occurrence
R	Crystal growth rate
r	Radius of curvature of cluster
r_c	Radius of curvature of critical cluster
S	Surface area
T	Absolute temperature
t	Time
U	Activation energy for volume diffusion of monomer
U_D	Activation energy for surface diffusion of monomer
U_{des}	Activation energy for desorption of monomer
U_E	Activation energy for the entry of a growth unit into a cluster
V	Volume of droplet
V_m	Molar volume of solute
v	Relative solution velocity
W	Probability of droplet nucleation
x	Number of molecules in a cluster
x_c	Number of molecules in a critical cluster
Z	Zeldovich factor
z	Coordinate normal to a crystal face

α_x	Cluster containing x molecules
β	Probability factor defined by equation (II-11)
γ	Cluster-solution interfacial free energy
γ_a	Binding energy for two-dimensional nucleation
δ	Boundary layer thickness
$\bar{\delta}$	Lattice parameter of surface
θ	Cluster-foreign surface contact angle
θ_2	Induction time for homogeneous nucleation
λ	Numerical factor defined by equation (I-10)
μ	Kinematic viscosity
ν	Frequency factor defined by equation (I-4)
ρ	Density of solute
σ	Relative supersaturation
σ_c	Characteristic parameter for dislocation theory
τ_1	Relaxation time to approach a steady-state cluster distribution
τ_2	Relaxation time to achieve the occurrence of a critical cluster
Φ	Cluster shape factor
Ω	Volume of solute molecule
$\bar{\omega}$	Vibrational frequency factor

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